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Hysteresis in Ce-based AB_5-type metal hydrides

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The effect of partial substitution of Ni in $Ce_{1-x}La_xNi_5$ intermetallic compound-hydrogen systems by Al, Sn and Co on hysteresis has been studied by pressure-composition-isotherm measurements. Al- and Sn-containing systems manifested a dramatic lowering of equilibrium pressures in comparison with their corresponding base compounds which can be attributed to higher Al and Sn atomic radii than that of Ni, and consequently, expanded intermetallic matrix. The addition of tin led also to widening of the α-region (solid solution) and shortening of the isotherm plateaus accompanied with significant reduction of hysteresis. The Co-substituted compositions were found to be of particular importance among $CeNi_5$-based systems because of their unique capability to reduce hysteresis without decreasing equilibrium pressures. This effect was due to nearly equal atomic radii of Ni and Co, and therefore, unaffected lattice parameters, and on the other hand, to the appearance of an intermediate hydride phase.

1. Introduction

Pressure hysteresis which is the difference between absorption and desorption equilibrium pressures, is a basic feature of most metal-hydrogen systems. Depending on chemical composition and pressure-temperature conditions, the hysteresis may attain a significant value that poses a serious problem of energy loss during absorption-desorption cycling. In spite of numerous experimental studies and theoretical models, the nature of this phenomenon is not yet completely understood and thus, the present level of knowledge does not allow, in general, adjusting hysteresis value selectively by varying alloy composition. This problem has a particular importance in the case of cerium-based AB_5 intermetallic compounds.

Among hydride forming alloys, AB_5 compounds of rare earth and d-metal with $CaCu_5$ structure type are often considered the most promising for various applications due to their high hydrogen absorption capacity, cyclic durability and resistance against impurities. An additional important feature of these compounds is the possibility to modify absorption-desorption equilibrium pressures within very large limits by partial substitution of A or B components without significant changes in hydrogen capacity. At the same time, cerium containing AB_5-type high-pressure hydrides are characterised by an extremely large hysteresis effect [1]. It has been established that the magnitude of the hysteresis in $CeNi_5$-based systems strongly depends on any variation of intermetallic matrix composition [2].

The effect of partial substitution of B-component (Ni) with various metals (Cu, Fe, Co, Mn, Al, Si and Sn) has been studied earlier [3–7]. However, a major part of experimental work on phase equilibria and hysteresis phenomenon in AB_5 hydrides has dealt with Mm-based systems [3–6] or alloys with high La-content and relatively low equilibrium pressures, e.g. [7]. Furthermore, the results obtained for $MmNi_{5-x}M_x$ cannot be considered a valid evidence of the influence of substitution elements on Ce-based hydrides. The main reason is the presence and variable amount of iron (up to 8 wt%) and other rare earth metals (approx. 40–50 wt%) in mischmetal which can change the stoichiometry of the alloys and thus, lead to appearance of secondary phases, as it has been shown in Ref. [8]. On the other hand, according to experimental results obtained for the $Ce_{1-x}La_xNi_5$-H_2 [9] and $Ce_{1-x}La_xNi_{5-y}Cu_y$-H_2 [2] systems, the critical temperature and thermodynamical behaviour change markedly with the variation of alloy composition. Consequently, regularities found, for example, for $Ce_{0.5}La_{0.5}Ni_{5-x}M_x$ [7] cannot be a priori extrapolated to systems with higher Ce-content, especially at elevated temperatures closer to critical values.

The present study is aimed at finding out Co-, Al- and Sn-substitution effects on the hydriding properties of Ce-rich $Ce_{1-x}La_xB_5$ compounds. In particular, the hysteresis values in the high-pressure range are investigated at two temperatures, 20 and 60 °C, close to the working ones of a multi-stage hydrogen compressor in a self-sufficient solar hydrogen energy system [10].

2. Experimental details

The alloys were prepared by arc melting under an argon atmosphere of the following raw materials: 99.9% purity cerium and lanthanum; 99.99% purity nickel, cobalt and tin; and 99.999% purity aluminium, except for $Ce_{0.7}La_{0.3}Ni_{4.5}Co_{0.5}$ which had been prepared earlier elsewhere by RF induction melting. Samples were remelted several times to ensure their homogeneity. Samples that lost less than 0.1% of their weight during melting were analysed by X-ray diffraction (XRD) and studied as cast. Powder XRD measurements were performed using a DRON-2 apparatus (Cu K_α radiation, Si-filter). The experimental device for alloy-hydrogen interaction study, allowing operation in a high-purity hydrogen atmosphere (99.9999%) at pressures up to 2000 atm, has been described earlier [11]. Pressure-composition isotherms (PCIs) were measured after degassing and two activating absorption-desorption cycles, in order to obtain reproducibility in sample behaviour [2].

Equilibrium parameters for $\alpha \to \beta$ (solid solution → hydride phase) and $\beta \to \alpha$ transformations were calculated at the composition of 3.0 hydrogen atoms per formula unit ($3H/AB_5$), corresponding approximately to the middle of the PCI plateaus. To evaluate hysteresis value and its temperature dependence, ratios of absorption pressure to desorption pressure (p_{abs}/p_{des}) at two temperatures were used. As a measure of the feasibility for applications, a compression factor—the ratio of desorption pressure at 60 °C to absorption pressure at 20 °C—of the studied alloy-hydrogen systems has also been calculated.

3. Results and discussion

3.1. Crystal structure, activation and hydriding properties

The composition and structure parameters of the studied compounds are presented in Table I. All prepared alloys were single-phase compounds crystallised in the hexagonal $CaCu_5$ structure type. No evidence of secondary phases was obtained from XRD patterns. It should be noted that there was no significant variation in unit cell volume for $Ce_{0.8}La_{0.2}Ni_{5-x}Co_x$ in a wide range of Co-concentration. On the contrary, even small additional substitution of Ce by La, and especially of Co by Sn, resulted in pronounced lattice expansion.

TABLE I Composition and X-ray diffraction parameters of starting alloys

	Structure parameters		
Alloy composition	*a* (nm)	*c* (nm)	$v \times 10^3$ (nm^3)
$Ce_{0.8}La_{0.2}Ni_5$	0.4915	0.4000	83.68
$Ce_{0.8}La_{0.2}Ni_{4.5}Co_{0.5}$	0.4913	0.4003	83.68
$Ce_{0.8}La_{0.2}Ni_{4.0}Co_{1.0}$	0.4917	0.4002	83.79
$Ce_{0.8}La_{0.2}Ni_{3.5}Co_{1.5}$	0.4920	0.3999	83.83
$Ce_{0.8}La_{0.2}Ni_{4.9}Al_{0.1}$	0.4920	0.4005	83.96
$Ce_{0.7}La_{0.3}Ni_{4.5}Co_{0.5}$	0.4929	0.3999	84.14
$Ce_{0.7}La_{0.3}Ni_{4.5}Co_{0.3}Sn_{0.2}$	0.4920	0.4031	84.50

The initial hydrogenation reaction in studied systems was characterized by very slow kinetics with long (30–60 min) incubation period, and a hydrogen pressure rise up to 200 atm was needed, except for the Sn-substituted alloy which was easily activated at 80 atm with short incubation period. The isotherms for the first activation cycle were not measured in detail, but it can be mentioned that both absorption and desorption equilibrium pressures differed remarkably from those at the second and further cycles. Similar reduction of hysteresis due to decrease of absorption pressure and increase of desorption pressure during activation has been observed previously for $CeNi_5$ and its derivatives [2]. During the subsequent PCI measurements, the kinetics was, in general, very slow and thus, needs to be improved in applications that require fast cycling.

The variation of alloy composition did not have a significant effect on absorption capacity. The maximum hydrogen content of the studied hydrides at room temperature was close to 6.5 H/AB_5 for all systems, regardless of the nature and concentration of the substituent. At the same time, there were significant changes in isotherm shapes (Figs 1–4) and in some thermodynamical parameters (Table II).

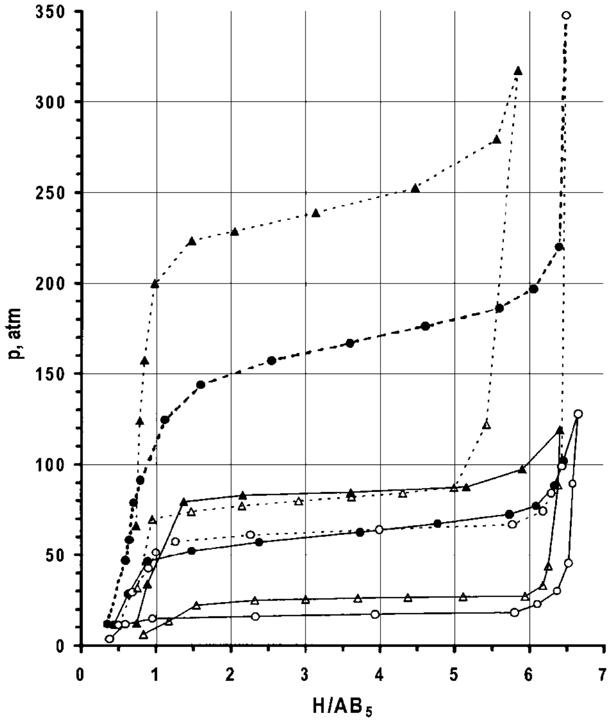

Figure 1 The absorption (closed symbols) and desorption (open symbols) isotherms for the $Ce_{0.8}La_{0.2}Ni_5$-H_2 (△) and $Ce_{0.8}La_{0.2}Ni_{4.9}Al_{0.1}$-$H_2$ (○) systems. Solid curves at 20 °C, dashed at 60 °C.

TABLE II Hysteresis values and compression factor for the studied AB_5-H_2 systems

Alloy composition	p_{abs}/p_{des} (20 °C)	p_{abs}/p_{des} (60 °C)	$p_{comp.}$
$Ce_{0.8}La_{0.2}Ni_5$	3.27	2.96	0.96
$Ce_{0.8}La_{0.2}Ni_{4.5}Co_{0.5}$	2.92	2.23	1.17
$Ce_{0.8}La_{0.2}Ni_{4.0}Co_{1.0}$	1.79	1.55	1.77
$Ce_{0.8}La_{0.2}Ni_{3.5}Co_{1.5}$	1.13	1.07	2.58
$Ce_{0.8}La_{0.2}Ni_{4.9}Al_{0.1}$	3.58	2.59	1.05
$Ce_{0.7}La_{0.3}Ni_{4.5}Co_{0.5}$	2.74	2.22	1.28
$Ce_{0.7}La_{0.3}Ni_{4.5}Co_{0.3}Sn_{0.2}$	1.68	1.60	2.13

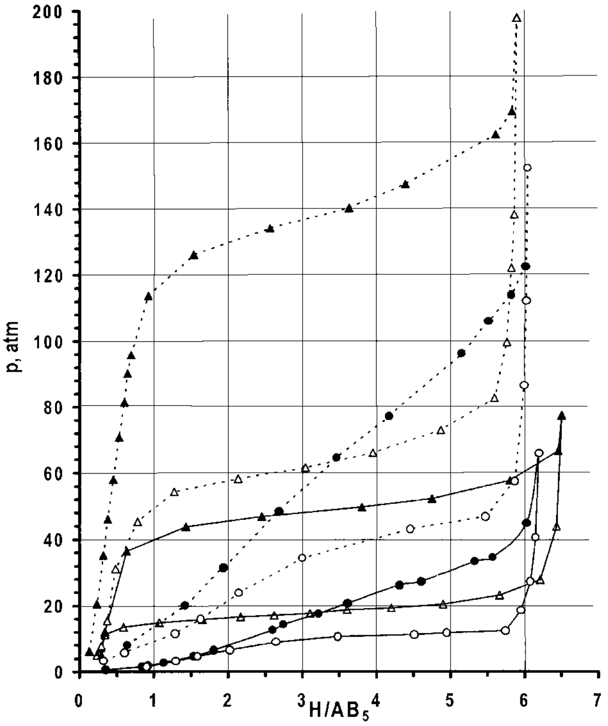

Figure 2 The absorption (closed symbols) and desorption (open symbols) isotherms for the $Ce_{0.7}La_{0.3}Ni_{4.5}Co_{0.5}$-$H_2$ (△) and $Ce_{0.7}La_{0.3}Ni_{4.5}Co_{0.3}Sn_{0.2}$-$H_2$ (○) systems. Solid curves at 20 °C, dashed at 60 °C.

3.2. Effect of Al

Pressure-composition isotherms of the $Ce_{0.8}La_{0.2}Ni_{4.9}Al_{0.1}$-$H_2$ system are presented in Fig. 1, together with those of the $Ce_{0.8}La_{0.2}Ni_5$-H_2 base system. Both systems are characterised by flat plateaus, but the Al-substituted system has a narrower α-region at 20 °C. It should also be noted that unlike in the Al-free system, there is no visible reduction of plateau length at 60 °C in the Al-substituted system. Taking into account the known correlation between changes in plateau length with temperature and proximity of the critical point in the phase diagram, this fact can be considered an evidence of an increase of the critical temperature with aluminium substitution.

The main effect of Al is a considerable lowering of the absorption and desorption pressures even at a very small partial substitution—2 at %. This effect is a common feature of all AB_5 metal hydrides (La- or Mm-based) and correlates with the higher radius of Al atom ($r_{Al} = 0.143$ nm) compared to that of Ni ($r_{Ni} = 0.124$ nm), and hence with the intermetallic lattice expansion (Table I).

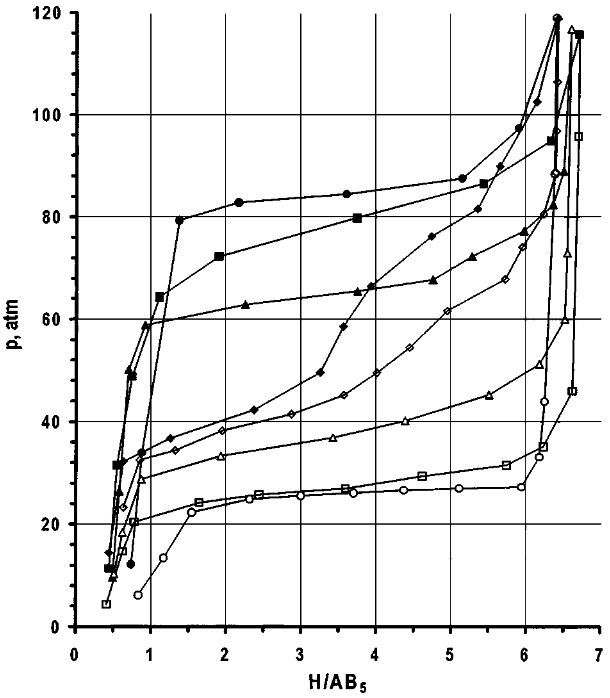

Figure 3 The absorption (closed symbols) and desorption (open symbols) isotherms for the $Ce_{0.8}La_{0.2}Ni_{5-x}Co_x$-$H_2$ systems at 20 °C; $x = 0$ (○), 0.5 (□), 1 (△), 1.5 (◇).

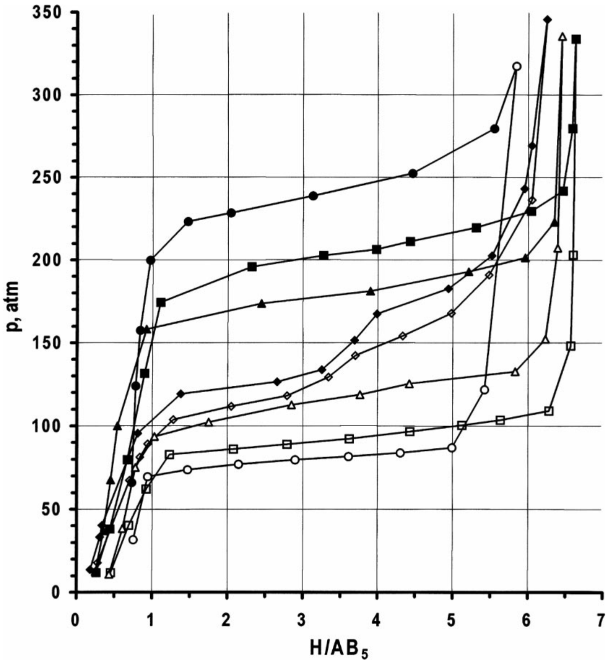

Figure 4 The absorption (closed symbols) and desorption (open symbols) isotherms for the $Ce_{0.8}La_{0.2}Ni_{5-x}Co_x$-$H_2$ systems at 60 °C; $x = 0$ (○), 0.5 (□), 1 (△), 1.5 (◇).

The results obtained in the present work seem to indicate that Al substitution leads to an increase of hysteresis at room temperature but to its reduction at 60 °C. This trend is evident in comparison with the closest Al-free composition $Ce_{0.8}La_{0.2}Ni_5$ (Table II) and even with the $CeNi_5$ base compound [2]. Such a pronounced temperature dependence of hysteresis contrasts with the data of Suda *et al.* [5] who have observed increase of hysteresis with temperature for $MmNi_{5-x}Al_x$ compositions. This remarkable difference between Mmand Ce-based systems (see also Ref. [9]) confirms that mischmetal components interfere strongly with the behaviour of metal-hydrogen systems and can induce significant changes in their general regularities.

3.3. Effect of Sn

Fig. 2 shows the absorption and desorption isotherms of the $Ce_{0.7}La_{0.3}Ni_{4.5}Co_{0.3}Sn_{0.2}$-$H_2$ and Sn-free $Ce_{0.7}La_{0.3}Ni_{4.5}Co_{0.5}$-$H_2$ systems. The decrease of equilibrium pressures with Sn-substitution is even more pronounced than in the case of Al, which can be attributed to the highest atomic radius ($r_{Sn} = 0.158$ nm) and the largest unit cell volume among the studied alloys (Table I). However, if the unit cell parameters of Al- and Sn-substituted alloys are compared to those of the corresponding Al- and Sn-free alloys, it can be observed that Al is more effective in increasing the cell parameters per equal amount of substitution (in at %).

The main difference between Al- and Sn-effects is a dramatic change of isotherm shapes in the case of Sn-containing system. One can see from Fig. 2 that the α-region is significantly widened and that the plateaus are badly sloping, especially for absorption. This phenomenon seems to be caused in part by some inhomogeneities in the cast alloy used in the present work. Similar behaviour of $MmNi_{5-x}Sn_x$ hydrides was effectively reduced after annealing, as has been observed by Mungole *et al.* [6]. The considerable plateau sloping does not allow us to carry out a true quantitative comparison of the calculated thermodynamical parameters between the $Ce_{0.7}La_{0.3}Ni_{4.5}Co_{0.3}Sn_{0.2}$-$H_2$ and the corresponding Sn-free system. However, it is evident that the hysteresis loop was markedly reduced with Sn-substitution at both 20 and 60 °C. Consequently, Sn-substitution improved the compression capability (Table II). Such a pronounced effect of Sn on the hysteresis magnitude is directly related to the isotherm shape and, hence, to the characteristics of phase equilibria in the system. According to most theoretical models of hysteresis in metal-hydrogen systems, its main origin is the strain of crystalline matrix during hydride formation and decomposition (see e.g. [12]). This strain is caused by the lattice volume expansion as the α-phase (solid solution) transforms into the β-phase (hydride). An extended α-region in the pressure-composition isotherm indicates that the difference in hydrogen content (and, certainly, molar volume) between α- and β-phases decreases and therefore, the strain of the lattice in the α-β transformations decreases, too. From this point of view, the effect of plateau shortening, such as the one observed in the present work for Sn-containing system, can be directly associated with the hysteresis decrease.

3.4. Effect of Co

The experimental data for a series of $Ce_{0.8}La_{0.2}Ni_{5-x}Co_x$ alloys with $x = 0$, 0.5, 1.0 and 1.5 are presented in Figs 3 and 4. They manifest a continuous reduction of hysteresis with increasing Co-content. This effect is due both to decrease of absorption pressure and to increase of desorption pressure. However, there exists a slight difference between equilibria in the system at 20 and 60 °C. This is more obvious from the curves in Fig. 5 in which the hysteresis values at both experimental temperatures are shown as a function of alloy composition. The p_{abs}/p_{des} vs. x dependence corresponding to 60 °C is practically linear, while at 20 °C, an irregularity at $x = 0.5$ is observed. The following explanation of this phenomenon could be proposed: A particular feature of the $Ce_{1-y}La_yNi_{5-x}Co_x$-H_2 system is the occurrence of two plateaus in the pressure-composition isotherms. This fact has been described earlier by Dayan and co-workers [7] for alloys with $y = 0.5$. The authors have considered the appearance of the second hydride phase the main reason to the reduction of hysteresis. In fact, division of one $\alpha \rightarrow \beta$ transformation with a large difference in hydrogen concentration between the solid solution and the hydride phase, into two separate reaction steps, shall reduce deformation strain in the crystal lattice. As it has been discussed above for the Sn-containing compound, such an effect, as a rule, leads to decreased hysteresis. In the present work on the $Ce_{0.8}La_{0.2}Ni_{5-x}Co_x$-$H_2$ system, we have no evidence of the existence of the intermediate hydride phase, except for the case of the highest studied Co-content ($x = 1.5$) which shows clearly two plateaus. On the basis of comparison with the $LaNi_5$-H_2 system in which the appearance of the intermediate hydride phase is more evident at high temperatures [13], we suggest (without proof for the time being) that the intermediate hydride phase in the $Ce_{0.8}La_{0.2}Ni_{5-x}Co_x$-$H_2$ system appears at high temperatures with lower Co-content than at low temperatures. In this case, different alloy behaviour at 20 and 60 °C would be quite reasonable. At $x = 1.0$ we cannot see two PCI plateaus at the applied temperatures, but the greatly reduced hysteresis would suggest the existence of the intermediate phase. We therefore propose that the two separate hydride phases do exist but that they are, at these temperatures, energetically so close to each other that visible difference in the plateau levels cannot be seen. In order to test these hypotheses, XRD and pressure differential scanning calorimetry (PDSC) studies are under way.

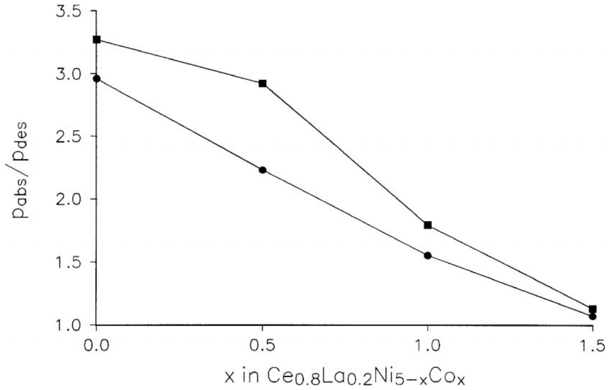

Figure 5 The hysteresis values (p_{abs}/p_{des}) in the $Ce_{0.8}La_{0.2}Ni_{5-x}Co_x$-$H_2$ systems at 20 °C (■) and 60 °C (●).

We also found some other contradictions with the data of Dayan *et al.* [7]. Firstly, we did not observe any significant loss of maximum hydrogen absorption capacity with increasing Co-content. Even at $x = 1.5$, the capacity exceeded 6 H/AB_5, while in Ref. [7], a decrease of hydrogen uptake to 4.5 H/AB_5 at $x = 1$ has been pointed out. Secondly, in contrast with the $Ce_{0.5}La_{0.5}Ni_{5-x}Co_x$-$H_2$ system in which the desorption pressure remained virtually unaffected by x-variation, in the present study, hysteresis was reduced through both absorption and desorption pressure changes. These features can obviously be attributed to the difference in the Ce/La ratio, and prove once more that there is no full analogy in the behaviour of the $Ce_{1-y}La_yNi_{5-x}M_x$-H_2 systems with varying value of y.

4. Conclusions

Partial substitution of Ni by Al, Sn or Co has a remarkable effect on the thermodynamical behaviour of Ce-rich AB_5-type alloy-hydrogen systems. Al and Sn containing systems manifested a dramatic lowering of equilibrium pressures in comparison with their corresponding base compounds. This effect is, as usual, due to higher Al and Sn atomic radii, expanded intermetallic matrix and consequently, higher stability of corresponding hydride phases. The alloy-hydrogen system with tin was characterised by reduced hysteresis which can probably be attributed to the observed widening of the α-region and shortening of the pressure-composition isotherm plateaus.

The Co-substituted compositions were found to be of particular importance among $CeNi_5$-based systems because of their unique capability to reduce hysteresis without decreasing equilibrium pressures. This effect, due to nearly equal atomic radii of Ni and Co, and therefore, unaffected lattice parameters, and on the other hand, to the appearance of an intermediate hydride phase, makes these systems, as far as the basic PCI properties are concerned, very promising for various high-pressure applications.

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