

HYDROGEN SORPTION BY THE METALLIC GLASS $\text{Ni}_{64}\text{Zr}_{36}$
AND BY RELATED CRYSTALLINE COMPOUNDS

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Introduction

In recent years much attention is paid to metal hydrides, especially because of their possible application in hydrogen-storage systems. Hydrides can also be used in hydrogen pumps and heat pumps. Such systems may be important in a future "hydrogen economy" (1).

In this paper we report on the hydrogen sorption characteristics of amorphous $\text{Ni}_{64}\text{Zr}_{36}$. A comparison will be made with crystalline eutectic $\text{Ni}_{64}\text{Zr}_{36}$, and with the intermetallic compounds $\text{Ni}_{10}\text{Zr}_7$ and Ni_5Zr_2 , because crystalline $\text{Ni}_{64}\text{Zr}_{36}$ consists of a mixture of these compounds. Amorphous alloys are of interest, because these may offer advantages over crystalline materials. The well-known hydride-forming compound LaNi_5 for example disintegrates into very small particles, which is technologically undesirable. Splat-quenched unhydrided alloys have a high yield stress and are ductile, contrary to intermetallic compounds and therefore may be less subject to disintegration.

Other physical parameters which are important in view of the applications mentioned above are the heat of formation of the hydride, the kinetics of hydrogen absorption and desorption, the possible changes of the surface layer of the material during hydrogen sorption and the influence of these changes on the kinetics (activation).

Experimental Details

The alloys investigated had the following nominal compositions: $\text{Ni}_{63.7}\text{Zr}_{36.3}$, $\text{Ni}_{58.9}\text{Zr}_{41.1}$ ($\text{Ni}_{10}\text{Zr}_7$) and $\text{Ni}_{71.3}\text{Zr}_{28.7}$ (Ni_5Zr_2). The preparation of the alloys and the method to measure the pressure-composition isotherms have been described in an earlier paper (2).

The heats of formation of the crystalline alloys were determined with a liquid-bath calorimeter (3). From the heats of solution in liquid Ge of Zr, Ni and the alloys mentioned above the heats of formation of the alloys were obtained.

The kinetics of the hydrogen sorption reaction was measured in two ways. (i) The pressure change during each step of the PC-isotherm measurements was recorded. (ii) The heat effect that occurred during hydriding was recorded with a calorimeter (Perkin-Elmer, DSC-2).

Results and Discussion

Phase Diagram near the eutectic $\text{Ni}_{64}\text{Zr}_{36}$ composition

There exists considerable confusion on the composition and structure of the intermetallic compounds adjacent to the eutectic composition $\text{Ni}_{63.7}\text{Zr}_{36.3}$. Table I shows some relevant data from the literature and in fig. 1 the part of the NiZr-phase diagram in concern, according to Elliott (4), is depicted.

TABLE I	
Literature Data of Phases on both Sides of eutectic $\text{Ni}_{64}\text{Zr}_{36}$	
Reference	Intermetallic compounds
Kirkpatrick and Larsen (5)	$\text{Ni}_{10}\text{Zr}_7$ and Ni_5Zr_2
Meny and Champigny (6)	Ni_3Zr_2 and Ni_3Zr
Kubaschewski (7)	$\text{Ni}_{10}\text{Zr}_7$ and Ni_2Zr

In addition Sweeney and Batt (8) report that they did not observe Ni_5Zr_2 in their diffusion experiments, but Pet'kov, Markiv and Gorskiy (9) did observe Ni_5Zr_2 in as-cast specimens. However, after annealing these specimens at 900°C for 200 hours the Ni_5Zr_2 phase had disappeared. To check the phase diagram we prepared specimens with nominal compositions $\text{Ni}_{10}\text{Zr}_7$, $\text{Ni}_{63.7}\text{Zr}_{36.3}$ and Ni_5Zr_2 . Microprobe investigation showed that the as-cast $\text{Ni}_{63.7}\text{Zr}_{36.3}$ sample consisted of a fine-grained mixture of $\text{Ni}_{10}\text{Zr}_7$ and Ni_5Zr_2 . The $\text{Ni}_{10}\text{Zr}_7$ sample consisted mainly of $\text{Ni}_{10}\text{Zr}_7$ but besides contained less than 2 percent of the eutectic mixture. The as-cast Ni_5Zr_2 sample consisted of three phases: a primary phase $\text{Ni}_{76.6}\text{Zr}_{23.4}$, a secondary phase Ni_5Zr_2 and thirdly an eutectoid mixture with overall composition $\text{Ni}_{59.1}\text{Zr}_{40.9}$. (This deviation from the eutectic composition may be due to the rapid cooling of the specimen). After annealing for 4 hours at 1030°C the sample consisted of Ni_5Zr_2 and for about 5% of $\text{Ni}_{10}\text{Zr}_7$. Further annealing this sample at 900°C during 215 hours caused no difference in the composition, in contradiction to the results of Petkov et al. mentioned above. But our results are in agreement with the phase diagram given by Elliott (4; fig. 1) and for the rest of this paper we consider Elliott's diagram as the correct one.

Pressure-Composition-Isotherms

Below a certain critical temperature the pressure-composition-isotherms of many hydride forming metals and alloys show a so-called pressure plateau: within a range of hydrogen concentration the pressure remains constant. Such a plateau corresponds with the coexistence of a saturated solution of hydrogen in metal, the α -phase, and a metal hydride, the β -phase. However, none of the isotherms of amorphous $\text{Ni}_{64}\text{Zr}_{36}$ (measured at 333 K, 433 K and 533 K) showed a pressure plateau (see figure 2).

This phenomenon can be due to a rather low critical temperature of amorphous $\text{Ni}_{64}\text{Zr}_{36}$ hydride or there may be no phase separation at all, even at low temperature. The low temperature range is difficult to investigate because of prohibitively long equilibration times. At room temperature for example the equilibration time amounted to several days, moreover no plateau was registered.

There is a clear difference between the hydrogen sorption behaviour of amorphous and crystalline

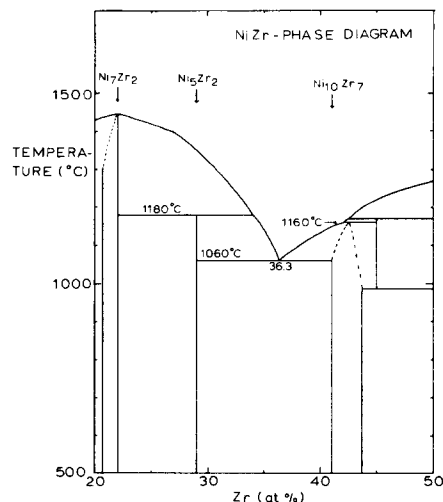


FIG. 1
Part of the Ni-Zr-Phase Diagram according to Elliott (4).

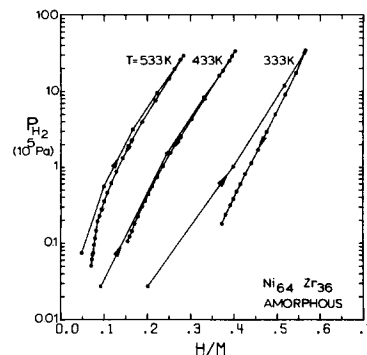


FIG. 2
Isotherms of amorphous $\text{Ni}_{64}\text{Zr}_{36}$ at 533 K, 433 K and 333 K.

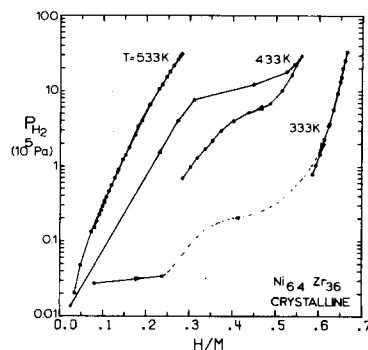


FIG. 3
Isotherms of crystalline $\text{Ni}_{64}\text{Zr}_{36}$ at 533 K, 433 K and 333 K.

$\text{Ni}_{64}\text{Zr}_{36}$ (compare figs. 2 and 3). Whereas the 533 K isotherms of both alloys are almost similar, the 433 K isotherm of crystalline $\text{Ni}_{64}\text{Zr}_{36}$ suggests the presence of a pressure plateau. Because of the limited number of data the existence of a plateau in the 333 K isotherm of crystalline $\text{Ni}_{64}\text{Zr}_{36}$ is not clearly defined but this isotherm differs considerably from the 333 K curve of amorphous $\text{Ni}_{64}\text{Zr}_{36}$. Our eutectic crystalline sample $\text{Ni}_{64}\text{Zr}_{36}$ consisted of $\text{Ni}_{10}\text{Zr}_7$ and Ni_5Zr_2 as discussed above. We therefore also measured the 533 K, 433 K and 333 K isotherms of $\text{Ni}_{10}\text{Zr}_7$ and the 433 K and 333 K isotherms of Ni_5Zr_2 (fig. 4). By adding 61.3% of the H/M ratio of $\text{Ni}_{10}\text{Zr}_7$ and 38.7% of this ratio of Ni_5Zr_2 at a number of pressures the dashed lines of figure 5 were constructed. The crosses representing the data on crystalline $\text{Ni}_{64}\text{Zr}_{36}$ are in good agreement with the dashed lines. So the pressure-composition-isotherms of crystalline (two phase) $\text{Ni}_{64}\text{Zr}_{36}$ are weighted averages of the isotherms of the single phases $\text{Ni}_{10}\text{Zr}_7$ and Ni_5Zr_2 .

For crystalline NiZr-alloys some data about the hydrogen sorption characteristics are available from the literature. Tannenbaum et al. (10) give values ranging from 0.9 to 1.1 for the maximum hydrogen to metal ratio of $\text{Ni}_{10}\text{Zr}_7$ -hydride at room temperature. We found a H/M-ratio of 0.9 at 333 K. The H/M-ratio's of crystalline $\text{Ni}_{64}\text{Zr}_{36}$ and Ni_5Zr_2 measured at 333 K are also somewhat smaller than the ratio's which Tannenbaum et al. found at room temperature.

Thermodynamics

From the P-C curves an estimation of the partial molar enthalpy of solution of hydrogen

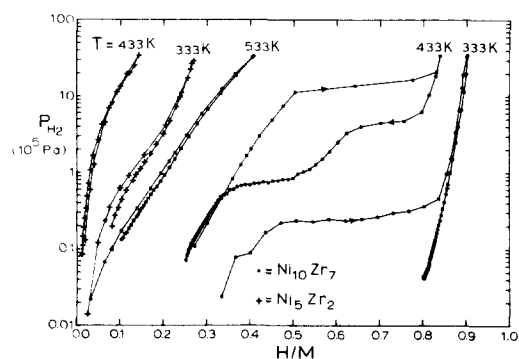


FIG. 4

Isotherms of $\text{Ni}_{10}\text{Zr}_7$ at 533 K, 433 K and 333 K and of Ni_5Zr_2 at 433 K and 333 K.

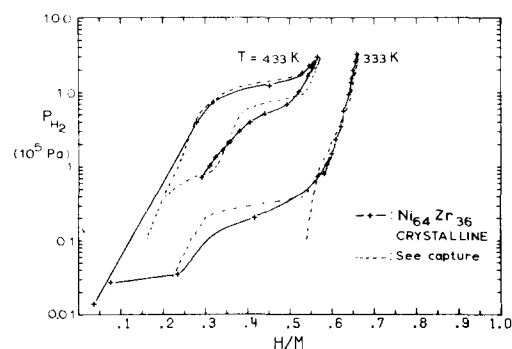


FIG. 5

Isotherms of crystalline $\text{Ni}_{64}\text{Zr}_{36}$ at 433 K and 333 K and the isotherms (dashed lines) constructed from the curves of Ni_5Zr_2 and $\text{Ni}_{10}\text{Zr}_7$ as described in the text.

and of the heat of formation of a hydride can be made. In case of hydride formation the dependence of the plateau pressure $P_{\text{H}_2}^*$ on the change in partial molar enthalpy ΔH° (heat of formation) and the change in partial molar entropy ΔS° per mole H_2 is described by $\ln P_{\text{H}_2}^* = \Delta H^\circ/RT - \Delta S^\circ/R$. In case of an ideal solution of hydrogen the formula $\ln P_{\text{H}_2} = \Delta H^\circ/RT - \Delta S^\circ/R + 2 \ln x_{\text{H}}$ holds with P_{H_2} the equilibrium pressure and x_{H} the number of dissolved H-atoms per metal atom. Assuming that ΔH° and ΔS° are independent of the temperature in a limited range, ΔH° can be calculated from a plot of $\ln P_{\text{H}_2}^*$ or $\ln P_{\text{H}_2}$ versus T^{-1} .

The values of ΔH° obtained in this way are compared in Table II with the values calculated from the alloy model developed by Miedema and coworkers (11-13). In this model it is assumed that upon the formation of a ternary hydride from a binary alloy B_nA , bonds between B and A atoms are broken by hydrogen atoms. It is supposed that A-A bonds do not occur in B-rich alloys. So in this cellular model, the heat of formation of the ternary hydride is taken to be the sum of the heats of formation of the two binary hydrides minus the heat of formation of the binary alloy B_nA (13); e.g.:

$$\Delta H^\circ(\text{B}_5\text{AH}_5) = \Delta H^\circ(\text{B}_5\text{H}_3) + \Delta H^\circ(\text{AH}_2) + \Delta H^\circ(\text{B}_5\text{A}) \text{ and}$$

$$\Delta H^\circ(\text{B}_3\text{AH}_4) = \Delta H^\circ(\text{B}_3\text{H}_2) + \Delta H^\circ(\text{AH}_2) - \Delta H^\circ(\text{B}_3\text{A}).$$

In a refinement on this theory (14) Miedema takes into account that frequently a number of A-A bonds will exist in the alloys with a higher A-content, and he corrects for this by subtracting only part of the heat of formation of the original alloys; e.g.:

$$\Delta H^\circ(\text{B}_2\text{AH}_{3.5}) = \Delta H^\circ(\text{B}_2\text{H}_{1.5}) + \Delta H^\circ(\text{AH}_2) - 0.7 \Delta H^\circ(\text{B}_2\text{A}) \text{ and}$$

$$\Delta H^\circ(\text{BAH}_{2.5}) = \Delta H^\circ(\text{BH}) + \Delta H^\circ(\text{AH}_{1.5}) - 0.5 \Delta H^\circ(\text{BA}).$$

For these calculations we require therefore the heats of formation of ZrH_2 , NiH , $\text{Ni}_{64}\text{Zr}_{36}$, Ni_5Zr_2 and $\text{Ni}_{10}\text{Zr}_7$. We used for the binary

hydrides of Zr and Ni values of -163 kJ/mol H_2 (15) and -8 kJ/mol H_2 (16) respectively. As mentioned above the heats of formation of $\text{Ni}_{64}\text{Zr}_{36}$, Ni_5Zr_2 and $\text{Ni}_{10}\text{Zr}_7$ were determined by liquid bath calorimetry. For the heat of formation of amorphous $\text{Ni}_{64}\text{Zr}_{36}$ we used the value of crystalline $\text{Ni}_{64}\text{Zr}_{36}$ minus the heat of crystallization of amorphous $\text{Ni}_{64}\text{Zr}_{36}$ (2). Table II shows the results obtained.

<u>TABLE II</u>			
Heats of Formation of binary Alloys, of ternary Hydrides as calculated from the PC-isotherms $\Delta H^\circ(\text{exp})$, and of ternary Hydrides as calculated from the Miedema-model, $\Delta H^\circ(\text{model})$.			
Alloy	$\Delta H^\circ(\text{exp})$ of binary alloy (kJ/mol)	$\Delta H^\circ(\text{exp})$ of ternary hydride (kJ/mol H_2)	$\Delta H^\circ(\text{model})$ of ternary hydride (kJ/mol H_2)
Ni_5Zr_2	-45 ± 4	-39 ± 4	- 20
$\text{Ni}_{64}\text{Zr}_{36}$ amorphous	-40 ± 5	-41 ± 4	- 48
$\text{Ni}_{64}\text{Zr}_{36}$ crystalline	-44 ± 4	-44 ± 6	- 48
$\text{Ni}_{10}\text{Zr}_7$	-48 ± 4	-47 ± 5	- 52

In view of the rather crude approximations made in the calculation of both experimental and theoretical ΔH° -values of the ternary hydrides, the agreement between the two sets of values is rather good. Only the Ni_5Zr_2 -values differ considerably. In this material however only a small amount of hydrogen is absorbed (fig 4) and therefore the Miedema-theory may not be applicable.

Disintegration

As already reported in (2), after a small number of hydriding-dehydriding cycles no disintegration of the amorphous $\text{Ni}_{64}\text{Zr}_{36}$ samples was observed. Also after 100 cycles (each cycle existing of one step to about 30 bar H_2 , and back to vacuum) at about 470 K the pieces of amorphous ribbon remained intact to a large extent. However after one further cycle at room temperature (295 K) most of the ribbon was fragmented into particles of 10 - 100 μm . This is a factor of ten larger than e.g. observed in LaNi_5 (16). But when the hydrogen pressure was increased by small steps, also at 295 K no disintegration occurred. Furthermore the group of Prof. Baranowski (17) applied a hydrogen pressure of 10 kbar at 420 K on samples provided by us. The resulting H/M ratio was 1.5, about twice as large as in our experiments. However, the samples did not disintegrate. We conclude that the stresses due to hydrogen absorption are higher during a fast and large pressure increase than during loading by small steps, and are also higher at room temperature than above. The incipient formation of an amorphous hydride phase at room temperature may be responsible for the disintegration.

Kinetics

Several processes take place during the hydriding of a material. Hydrogen molecules are adsorbed on the surface of the sample and dissociated into hydrogen atoms. These atoms are then absorbed in the first layers of the samples and diffuse into the bulk of the material. Each of these processes can be the rate-limiting step for the absorption of hydrogen. In the case of $\text{Ni}_{64}\text{Zr}_{36}$ we were not able to find a satisfactory model (e.g. diffusion controlled) to describe the absorption process, but it was clear that surface processes are of great importance. For example, the samples had to be "activated" before they could absorb hydrogen. Activation could be achieved in several ways. One way is to heat the samples in a hydrogen atmosphere. In the differential scanning calorimeter during heating of amorphous $\text{Ni}_{64}\text{Zr}_{36}$ at a rate of 40 K/min, the exothermic heat effect caused by the absorption of hydrogen started only at 600 K. A minor improvement was found by etching a sample (in a weak HCl solution) in order to remove an oxide layer, or by plating the surface of a sample with a Pd layer (in a PdCl_2 solution). The best preparation method was to grind the as-quenched samples, in which case hydrogen absorption started already at 400 K in the DSC. If after the absorption of hydrogen the purge gas of the DSC was changed from hydrogen to argon, desorption of hydrogen was observed. Below 470 K the desorption of hydrogen was not complete: at increasing the temperature, more hydrogen evolved from the sample. Repeating the procedure of (partially) hydriding and dehydriding it

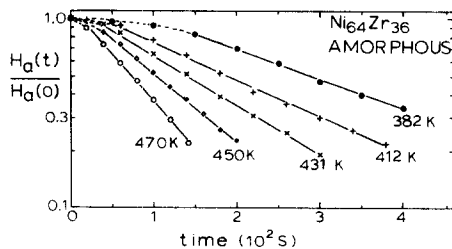


FIG. 6

The heat of absorption of hydrogen by amorphous $\text{Ni}_{64}\text{Zr}_{36}$ as function of time and temperature.

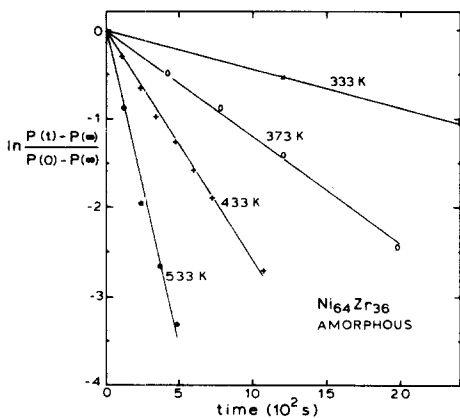


FIG. 8

The pressure drop during the hydriding of amorphous $\text{Ni}_{64}\text{Zr}_{36}$ as function of time and temperature.

plot of $\ln(p(t) - p(\infty))$ against t was made where $p(t)$ is the hydrogen pressure at time t and $p(\infty)$ the equilibrium pressure. As a measure for the absorption rate the mean slope of the first 30% of the pressure drop was used. The absorption rate increased considerably during the first 3 sorption cycles and much less during the next cycles. Six of the data points (marked with a different symbol) were obtained after opening the reaction vessel or after prolonged pumping. Probably in these cases the sample was oxidized slightly.

The absorption rate was determined at 533 K, 433 K, 373 K and 333 K. In fig. 8 the logarithm of the relative decrease of the pressure, $\ln((p(t) - p(\infty))/(p(0) - p(\infty)))$, with time is shown. The slope of these curves was plotted logarithmically against $1/T$. From this Arrhenius plot the value of the activation-energy was estimated at 20 ± 5 kJ/mol, which is in reasonable agreement with the value of 25 ± 3 kJ/mol found by calorimetry.

Conclusions

- The isotherms of amorphous $\text{Ni}_{64}\text{Zr}_{36}$ do not show a pressure plateau within the temperature range investigated, in contrast with the crystalline compounds $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Ni}_{10}\text{Zr}_7$. Apparently the critical temperature of amorphous $\text{Ni}_{64}\text{Zr}_{36}$ is lower than that of crystalline $\text{Ni}_{10}\text{Zr}_7$. Ni_5Zr_2 absorbs a relatively small amount of hydrogen.

- Amorphous $\text{Ni}_{64}\text{Zr}_{36}$ is much less subject to disintegration due to hydrogen sorption than comparable crystalline compounds.

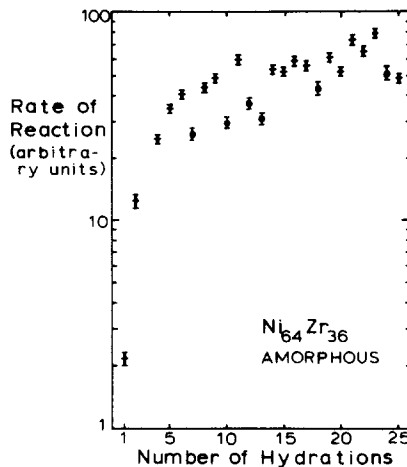


FIG. 7

The hydrogen absorption rate as function of the number of hydrations. For the meaning of the symbols see the text.

was noticed that the sorption rate increased steadily. Only after about 15 cycles the rate was constant. The time dependence of the heat effect during absorption of hydrogen at 5 temperatures between 380 K and 470 K is shown in fig. 6. Using only the straight parts of the curves of figure 6, the activation energy of the absorption process was estimated at 25 ± 3 kJ/mol.

The absorption rate of amorphous $\text{Ni}_{64}\text{Zr}_{36}$ samples was determined also by monitoring the pressure drop. In this case the activation of the samples was induced by cycling between a H_2 pressure of about 3MPa vacuum (1Pa) at an elevated temperature (370 K - 530 K). Here also the absorption rate increased with the number of absorption-desorption cycles as can be seen in figure 7. This figure shows the absorption rate as a function of the number of cycles. A

- From the PC-curves the heats of formation of the "hydrides" of amorphous $Ni_{64}Zr_{36}$ and the related crystalline compounds are found to be about 43 kJ/mol H_2 . Except for Ni_5Zr_2 this is in reasonable agreement with the values found by applying the Miedema model.

- It is not clear which of the processes that take place during hydrogen absorption is rate limiting. The activation energy of this process is found to be 25 ± 3 kJ/mol by calorimetry and 20 ± 5 kJ/mol by pressure measurements.

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References

1. F.E. Lynch, E. Snape, Proc. 2nd World Hydrogen Energy Conference, Zürich, p. 1475, Pergamon Press (1978).
2. F.H.M. Spit, J.W. Drijver and S. Radelaar, Zeitschrift für Physikalische Chemie Neue Folge, Bd 116, S225 (1979).
3. K. Tang and R. Castanet, J. Less Common Metals 51, 125 (1977).
4. R.P. Elliott, Constitution of Binary Alloys, 1st Suppl., McGraw Hill (1965).
5. M.E. Kirkpatrick and W.L. Larsen. Transactions of the ASM, Vol 54 (1961) 580.
6. L. Meny, M. Champigny, CEA-R-3517, Serv. Centr. de Doc. du CEA (1968).
7. O. Kubaschewski (ed.), Atomic Energ. Rev. Special issue no. 6.
8. W.E. Sweeney, Jr. and A.P. Batt, J. Nucl. Mat. 13, no. 1 (1964) 87.
9. V.V. Pet'kov, V.Ya. Markiv and V.V. Gorskiy, Russ. Metallurgy (1972) 137.
10. I.R. Tannenbaum, W.L. Korst, J.S. Mohl and G.G. Libowitz. 144th meeting of the Amer. Chem. Soc., Los Angeles, Calif., April 1963 (NAA-SR-7132).
11. A.R. Miedema, R. Boom, F.R. de Boer, J. Less Common Metals 41, 283 (1975).
12. A.R. Miedema " " " " 46, 67 (1976).
13. A.R. Miedema, K.H.J. Buschow, H.H. van Mal " " 49, 463 (1976).
14. A.R. Miedema, private communication.
15. D.R. Frederickson, R.L. Nuttal, H.E. Flotow and W.N. Hubbard, J. Phys. Chem. 67, 1506 (1963).
16. H.H. van Mal, Thesis Technical University Delft (1976).
17. B. Baranowski, private communication.