

STUDY OF CATALYSTS FOR FUEL CELL ELECTRODES. XVI.*

INFLUENCE OF PHASE COMPOSITION
OF NICKEL-ALUMINUM ALLOYS
ON ELECTROCHEMICAL PROPERTIES
OF NICKEL CATALYSTS

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Dedicated to the 65th anniversary of the late Academician R. Brdička,

The activity of nickel catalysts for anodic oxidation of hydrogen, prepared from pure phases NiAl_3 , Ni_2Al_3 , and their mixture, was studied. An addition of 2% of Ti, which proved to be the optimum quantity, raised the activity of the catalysts prepared from either phase to such an extent that the effect of the initial phase composition of the alloy was completely overridden.

Utilizing Raney nickel, prepared from alloys¹ Ni-Al, as an electrochemical catalyst promoting the ionization of hydrogen in three-phase gas electrodes has already been suggested. In Ni-Al equilibrium alloys, the following intermetallic components were clearly identified²: Ni_3Al , NiAl, Ni_2Al_3 , and NiAl_3 . The former two compounds are very stable in alkaline hydroxide solutions and are, therefore, not suited for preparing nickel catalysts³. Ni_2Al_3 and NiAl₃ on the other hand yield a catalyst with a highly developed surface because the removal of aluminum by leaching in alkaline hydroxides presents no difficulties. In practice, however, all the phases quoted may appear, depending on the composition and the mode of preparation of the alloy. As has already been reported by Justi¹, the alloy 50 Ni/50 Al is most suitable for electrochemical purposes; this alloy consists of the phases NiAl₃ and Ni_2Al_3 and of an eutectic NiAl₃-Al. Due to the fact that no pure phase but a mixture is involved, efforts have been made^{4,5} to determine which of the two phases was responsible for the electrochemical catalytic activity. Since a certain analogy may be expected to exist between the electrochemical activity of the Raney nickel and its hydrogenating action in heterogeneous chemical catalysis⁶, some conclusions concerning the individual phases may also be drawn from other than electrochemical studies³.

The foregoing papers, however, do not lead to a unanimous conclusion with respect to the electrochemical activities of the individual phases. Jandera and coworkers⁵, for instance, report that differences due to the varying ratio of the phases NiAl₃ and Ni_2Al_3 are not so pronounced, as to provide a sound basis for determining the individual contributions to the activity. Stempel⁴, on the contrary, designated the phase NiAl₃ as the one to possess an extra activity for preparing the Raney nickel. Sas-

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soulas and Trambouze³ studied the catalytic hydrogenating activity of catalysts prepared from pure phases NiAl_3 and Ni_2Al_3 , the Ni_2Al_3 phase proving to be the more active one. As it is possible to prepare the pure phases NiAl_3 and Ni_2Al_3 by reaction of the components in the appropriate ratios and by their potential subsequent heat treatment, it is the subject of the present paper to study the activity of the electrochemical catalysts prepared from them. The properties of the electrochemical catalysts may be promoted by adding titanium⁷; the influence of an addition of this metal to the catalysts prepared from pure phases has, therefore, also been studied.

EXPERIMENTAL

Preparation of Alloys

The alloys Ni-Al, if required containing also Ti, were prepared by powder metallurgy⁴ and by melting.

When preparing from powders, carbonyl nickel powder (USSR PNK-2, GOST 9722-61), passed through a 40 μm sieve, was employed. The other component used was aluminum powder of inland make, trade mark Albo, 99.5% purity grade, grain size under 63 μm . Both powders were mixed in a ratio corresponding to the phase composition of NiAl_3 and Ni_2Al_3 , respectively, in such a way that the aluminum powder was admixed to a sludge consisting of the nickel powder and acetone. In this way it was possible to overcome the difficulties which are otherwise encountered when dry-mixing powders of such a difference in specific densities, and a homogeneous mixture was obtained. After mixing, the acetone was evaporated at room temperature. The dry mixture was then used for pressing compacts of approximately 1 mm thickness and 30 mm diameter by a pressure of 1500 kg/cm^2 , in a steel die. The green compacts were then placed into a quartz tube in a nickel plate holder approximately 1 mm apart and heated in a stream of dry electrolytic hydrogen (from which oxygen had been removed by a layer of copper filings at 400°C). The heating regime consisted of a period of about 15 minutes, during which the temperature reached 400°C, then of a period of further 4 hours during which the temperature increased linearly up to

TABLE I

Composition and Mode of Preparation of Phases NiAl_3 and Ni_2Al_3 and Catalysts Prepared from Them by Leaching

No	Alloy		Alloy		Catalyst	
	Composition	Mode of preparation	Ni, %	Al, %	Ni, %	Al, %
1	Ni_2Al_3	powder metal.	58.9	40.7	65.6	21.3
2	Ni_2Al_3	melting	60.3	40.6	67.9	9.8
3	$\text{Ni}_2\text{Al}_3 + 2\% \text{Ti}$	melting	58.6	37.4	58.6	20.9
4	NiAl_3	powder metal.	41.8	56.8	70.7	6.6
5	NiAl_3	melting	40.0	58.7	75.5	2.4
6	$\text{NiAl}_3 + 2\% \text{Ti}$	melting	41.5	53.1	69.1	5.5

TABLE II
Alloys 50 Ni/50 Al with Varying Content of Ti and Catalysts Prepared from Them

Alloy No	Alloy			Catalyst		
	Ni, %	Al, %	Ti, %	Ni, %	Al, %	Ti, %
7	47.7	52.3	0	77.0	4.0	0
8	48.5	51.1	0.35	73.1	5.0	0.65
9	49.3	48.6	2.05	69.5	6.3	3.55
10	49.2	44.9	5.9	53.6	14.5	8.48

620°C. At this temperature, a visible exothermal reaction set in with the consequence of a sudden increase in the temperature. The reaction between the nickel and aluminum occurred, however, also at temperatures below 600°C as was concluded from the fact that a long-term heating to temperatures below the quoted limit brought the reaction to its end-point without the exothermal effect mentioned previously. After the decay of the exothermal reaction, the furnace was switched off and left to cool spontaneously for about two hours, still under hydrogen stream.

The melting of the alloys was carried out in a vacuum induction furnace which permitted the preparation of samples up to a volume of 500 ml. The melt was held in magnesite crucibles. Electrolytic nickel and aluminum of a 99.99% purity grade and titanium of a purity above 99.99% were employed as the initial materials. Samples corresponding to the composition of 500 g of the respective alloy were placed into the crucible, the melting space was evacuated to $3 \cdot 10^{-2}$ Torr, and 100 Torr of argon was let in. The sample was then carefully heated up to 1500°C until complete liquefaction was achieved which occurred after 5–10 minutes. The temperature was controlled with an electric pyrometer. The alloys prepared were let to cool spontaneously in an argon inert atmosphere, as mentioned previously. The composition of the alloys was subsequently controlled by chemical analysis (by complexometry). The results are summarized in Tables I and II.

Some of the alloys were heat-conditioned with the aim of increasing their phase homogeneity; they were heated to 600°C for a period of 70 hours in an atmosphere of electrolytic hydrogen which had previously been freed from oxygen (Cu, 400°C) and moisture (molecular sieve Nalsit 4).

The phase composition was controlled by investigating metallographical ground section etched with 6M-KOH at room temperature for 20 seconds⁴ and by qualitative X-ray structural analysis.

Preparation of Catalysts

The alloys prepared by powder technology in the form of compacts were easily pulverized in a porcelain pulverizing dish to pass through a 40 µm sieve. The alloys obtained by melting were mechanically crushed and ground in a steel vibrating mill, passed through a 40 µm sieve, and the coarse fractions returned to the mill until 95% of the initial quantity passed through the sieve. The powdered alloys thus obtained were leached in 5M-KOH at 90°C. After the leaching was finished the suspension was neutralized with a 10% solution of tartaric acid up to a 6.6 pH end-point; the catalyst obtained was then thoroughly washed with hot distilled water and dried in air at room temperature. The preparation procedure has in detail been described previously⁸. The chemical composition of the dry catalysts was determined by complexometry (Table I). The grain

size distribution of both the alloys and the catalysts was measured on an automatic sedimentation balance Sartorius 4600.

Determination of Electrochemical Activity

The electrochemical activity was evaluated on the basis of polarization curves. The dependence of the polarization of the hydrogen electrodes, containing the catalysts to be tested, on the anodic current of hydrogen ionization was measured with the aid of disc-shaped five-layer double-faced electrodes of $2 \times 5 \text{ cm}^2$ total geometric operating surface area. The electrode material was classified carbonyl nickel (USSR, GOST 9722-61 PNK-2) fraction below $40 \mu\text{m}$. Electrodes were pressed by 1500 kg/cm^2 and sintered in a hydrogen atmosphere at 450°C for $1\frac{1}{2}$ hours, as has already been described⁹. A special attention was paid to the preparation process of the electrodes due to the fact that it is of a major importance for the reproducibility of the results.

The catalytic layers of the electrodes were 0.13 cm thick and contained 9 parts by weight of carbonyl nickel and 1 part by weight of the dry catalyst, the mixture having already proved suitable for testing the electrochemical activity of catalysts¹⁰. This dilution of the catalyst with carbonyl nickel, which at 25°C has a negligibly low activity, resulted in an increase of the current density per unit of the true surface area of the catalytic skeleton so that differences in the catalyst activities became more appreciable. The catalytic skeleton consisted of 62% by volume of the porous metal phase containing pores of $2 \mu\text{m}$ diameter and of 38% by volume of pores of 40 to $60 \mu\text{m}$ which were prepared with the aid of a pore forming agent.

The electrochemical measurements were carried out in 7M-KOH at 25°C and at 0.8 atm of electrolytic hydrogen by the usual method of imposed controlled current. The potential was measured against a Hg/HgO reference electrode containing also 7M-KOH. The potential value, corresponding to a given current load, was read off after stabilization of the value (change of the potential with time below 0.2 mV/min). With an increase in the current density the stabilization took longer until, from a certain current density value on, the stabilization did not take place at all and the potential of the electrode shifted to the value of the corrosion potential of nickel. Such measurements were not included in the results quoted.

RESULTS AND DISCUSSION

The alloys employed for investigating the catalytic activities of pure and with Ti doped phases Ni_2Al_3 and NiAl_3 are summarized in Table I. The phases quoted are the principal components of nickel and aluminum alloys destined for preparing catalytic Raney nickel. The usual composition of commercially available alloys is 50 Ni/50 Al. Pulverization of cooled alloys to grains below $40 \mu\text{m}$ proved very tedious. For this reason efforts were made to prepare alloys 1 and 4 by interaction of powdered components. This procedure yielded an alloy of the required composition in an extremely porous form and of a low mechanical strength which could easily be crushed. For reaching the mentioned low mechanical strength, the heating regime had to be controlled in such a way to prevent liquefaction of the components. Although, from the technological point of view, the facility of preparing powdered alloys is most important, its high porosity before grinding was highly inconvenient for the metallographic evaluation of the alloys.

Ground sections prepared from these samples did not allow a unanimous determination of their phase compositions, the metal phase surface areas on the porous

material being too small to reveal the design characteristic for the individual phases. For this reason it was extremely difficult to draw conclusions as to the homogeneity of the sample. When in some cases larger areas were found, it was observed that the sample in these places did not contain only one phase, not even after 200 hours heat conditioning. The fact that heat conditioning did not lead to visible changes may be explained by a hindered diffusion in the porous system of these samples as compared to the compact castings. This uncertainty, of course, reduced the value of these samples from the electrochemical properties investigation point of view.

Qualitative X-ray structural analysis proved that the major part of the sample was formed by a pure phase which, however, was accompanied by a certain quantity of other phases or pure metals. The fact, however, that the samples 1 and 4 yielded results identical with verified pure phases 2 or 5 (which were prepared by melting — see Fig. 2) suggests that alloys 1 and 4 were also predominantly pure phases Ni_2Al_3 and NiAl_3 .

Chemical analysis of the alloys revealed that in all cases the composition was close to theory (Ni_2Al_3 contains in theory 59.2% Ni and 40.8% Al; NiAl_3 contains theoretically 42.04% Ni and 57.96% Al) Ti being added at the expense of Al. Aside from the components contained in Table I (Raney nickel and residual aluminum), the leached and dried catalyst contained also chemically bonded oxygen and water, in the form of a surface passivating layer, which was the cause of its unpyrophority⁸.

The residual aluminum content varies considerably from one leached alloy to the other. When comparing alloys of an equal composition obtained by melting and by powder metallurgy, the Al content of the latter is higher which may be attributed to the presence of phases insoluble in KOH. Alloys containing Ti exhibited also a higher content of the residual Al in comparison with alloys of the same composition but without Ti (both alloys prepared by melting). As may be seen from Table II, the increase in the unleached Al content is evidently due to the increase in the quantity of Ti added to the alloy.

For comparing the electrochemical catalytic activity of various catalysts, it is important that the grain size distribution of the catalysts be equal in all the cases tested. In a porous three-phase electrode, the activity of the surface is determined by the degree of its coverage with the catalyst, unless the generated current is limited by other factors as for instance the electrolyte resistance, the active gas transport, the electrode reaction products diffusion, *etc.* The degree of coverage with the catalyst is proportional to the shape and number of the catalyst particles per unit weight. If the catalytic activity of highly active catalysts is to be determined, only a small quantity of the catalyst is to be incorporated into the supporting nickel skeleton in order that the specific current density per unit of the true catalyst surface area be sufficiently high, and that the current drawn be not limited by another of the above quoted factors, but solely by its catalytic activity. This was attained by a proper dilution of the catalyst with non-catalytic material¹⁰, in our case with carbonyl nickel powder.

This dilution underlines the importance of an equal grain size distribution in all the samples compared, in order that a constant ratio between the catalytic and

non-catalytic portion of the surface be ensured. It may be seen from the distribution curves (Fig. 1) of the alloys and catalysts prepared from them that this requirement was met. Fig. 1 depicts, for the sake of simplicity, only the extreme values: the finest and the coarsest samples of the powdered alloys quoted in Tables I and II. All other samples of both the alloys and catalysts prepared fall into the region defined by the two curves. The fact already found before¹⁰ was again confirmed that the grains of the alloys were not desintegrated by leaching.

Fig. 2 depicts the curves polarization-current density as a measure of the catalytic activity of hydrogen electrodes containing leached alloys 1-6 (Table I) and alloy 7 from Table II as catalysts. The values were obtained at 25°C; at this temperature, the catalytic activity of that part of the skeleton surface of the catalytic active layer, which is formed by carbonyl nickel, is negligible so that the activity of the electrode is due solely to the catalyst. The higher the activity of the catalyst, the lower at the given current density the polarization of the electrode. Current densities drawn from the electrodes at a constant polarization may be taken as a measure of this activity. For comparing the activities of various catalysts it is best to consider that portion of the polarization curve in which its dependence on the current density is close to linear. In the regions of a higher polarization, the course of the curves may be influenced by other effects than the activity of the catalyst (the current ap-

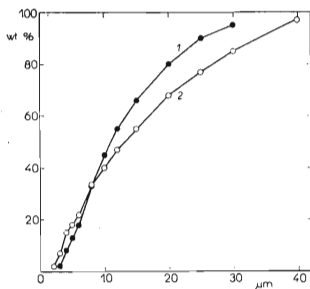


FIG. 1

Typical Grain Size Distribution Curves of Powdered Alloys Ni-Al

- 1 Alloy $\text{NiAl}_3 + 2\% \text{Ti}$ (see Table I, No 6);
2 alloy Ni_2Al_3 (see Table I, No 2).

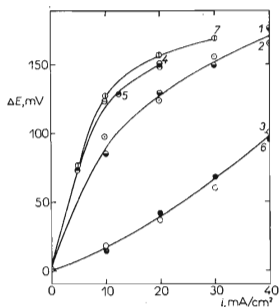


FIG. 2

Influence of Phase Composition on the Electrochemical Activity of Catalysts Prepared from Alloy Ni-Al and Ni-Al-Ti

Numbers are identical with Tables I and II; 7M-KOH, 25°C, $\Delta p_{\text{H}_2} = 0.8 \text{ atm}$.

proaching the limiting value, the dependence of the rate of the electrode reaction on the potential, *etc.*) and it is, therefore, not suitable for comparing the activities. The activities of the catalysts at a polarization of 50 mV are compared in Figs 2 and 3. It may be observed from Fig. 2 that the catalytic activity of the phase Ni_2Al_3 (curves 1 and 2) for the anodic oxidation of hydrogen is somewhat higher than that of the phase NiAl_3 (curves 4 and 5), irrespective of the mode of preparation of the initial alloy. Curve 7 pertains to a catalyst prepared from an alloy 47.7 Ni/52.3 Al, which contained, according to a qualitative investigation of its ground section, mostly the phase NiAl_3 aside from the phase Ni_2Al_3 and an eutectic NiAl_3 -Al.

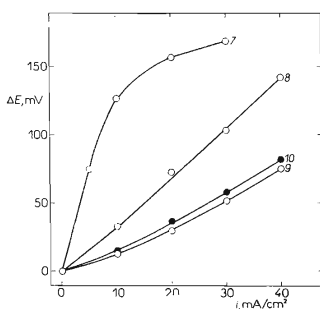
For this reason, the curve 7 is identical with curves 4 and 5 and the contribution of the phase Ni_2Al_3 did not, in the limits of accuracy of our measurements, make itself apparent. The addition of 2% of Ti to the phases under study (alloy 3 and 6, Table I) resulted in an eightfold increase of the catalytic activity as compared to catalysts 4, 5, and 7, and about a fivefold increase as compared to catalysts 1 and 2; the initial difference between the activities of the pure phase catalysts disappeared. Curves in Fig. 2 compare the catalytic activities per unit weight of the catalysts, their weights per 1 cm^2 of the catalytic skeletons being equal. Their activities may, however, be related to the unit weight of nickel due to the fact that their Ni content varies, in a certain range, from one case to the other (see Table I). In that event, the activity of the catalyst prepared from alloy 3 would be by approximately 18% higher as compared to the catalyst prepared from alloy 6 whose nickel content is higher.

It may be concluded from the results in Fig. 2 that after leaching the phase Ni_2Al_3 yields a catalyst somewhat more active than the phase NiAl_3 ; from the technological point of view, however, this difference, when considered for preparing catalysts for fuel cell electrodes, is of no importance because a small addition of some metals (*e.g.* Ti) can increase the catalyst activity considerably more.

FIG. 3

Influence of Addition of Ti on the Electrochemical Activity of Catalysts Prepared from Alloys Ni-Al

Numbers are identical with Table II;
7M-KOH, 25°C, $\Delta p_{\text{H}_2} = 0.8 \text{ atm.}$



To determine the optimum quantity of Ti dopant for the alloys 50% Ni + 50% Al, a series of these alloys was prepared containing up to 5.9% of Ti as may be seen from Table II. The initial content of Ti found in the alloy increased after leaching of aluminum. As has already been mentioned, an increase in the Ti content resulted in an increase of the residual aluminum. To enable a better understanding of the influence of Ti as an agent increasing the activity, its content in the catalyst in Table II was converted to values virtually existing in the working layer of an operating electrode (the reduced species of the catalyst, assumed in an operating electrode, was taken as 100%). The analytical data in Table II regarding the nickel and aluminum contents concerned their contents in a catalyst which also contains elements forming the passivating protective layer already mentioned. The results of measurements of the dependence of the polarization on the current density of hydrogen electrodes containing equal quantities by weight of the catalysts obtained by leaching alloys 7–10 (Table II) are contained in Fig. 3. If current densities at 50 mV are taken as a measure of the catalyst activity, a positive influence of an addition of Ti on the anodic oxidation of hydrogen may be observed in quantities up to 2% of the initial alloy. A further increase of the Ti content was of no practical importance. With an addition of 2% Ti, the alloy 9, which was a mixture of the phases Ni_2Al_3 and NiAl_3 exhibited an activity which was identical with the activity of either of the pure phases containing 2% of Ti (Fig. 2, curves 3 and 6).

It may be drawn from these results that when preparing technologically important catalysts, for instance catalysts for fuel cell electrodes, the difference in the activities of the individual phases is overridden by the pronounced influence of small additions of some metals, e.g. Ti, so that the phase composition of the Ni–Al alloy no longer influences the activity of the resulting catalyst.

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