

# Large-Scale Production and Quality Assurance of Hydrogen Storage (Battery) Alloys

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The new generation of high-capacity metal hydride rechargeable batteries is a cadmium-free energy alternative to current types of accumulators. While the first steps were made for consumer wireless applications, the newest developments aim toward traction systems (zero-emission cars). This article introduces the materials selection, quality control, and production principles of alloy systems suitable for storing hydrogen either electrochemically or by gas absorption. Examples of Zr-Ni, Ti-Mn<sub>2</sub>, and rare earth-Ni<sub>5</sub> are demonstrated from the metallurgical standpoint. These alloys (currently produced in large scale—tons/day) are now used in industry after approximately 20 years of development.

## Keywords

energy storage, hydrides

## 1. Introduction

THE use of electrode materials in rechargeable batteries shows an irreversible tendency from Cd- toward Ni-hydride compounds. The main reason for this anticipated strong restriction is environmental pressures, but also technical advantages, which allow longer operation times and miniaturization of equipment. The present hydride compounds are alloys based on Re (NiCo)<sub>5</sub>. They are being optimized continuously, and eventually on a medium-term basis, they will be supplemented by new alloys (e.g., monophasic AB<sub>2</sub> types) with less self-discharge, higher capacity, or improved corrosion resistance.

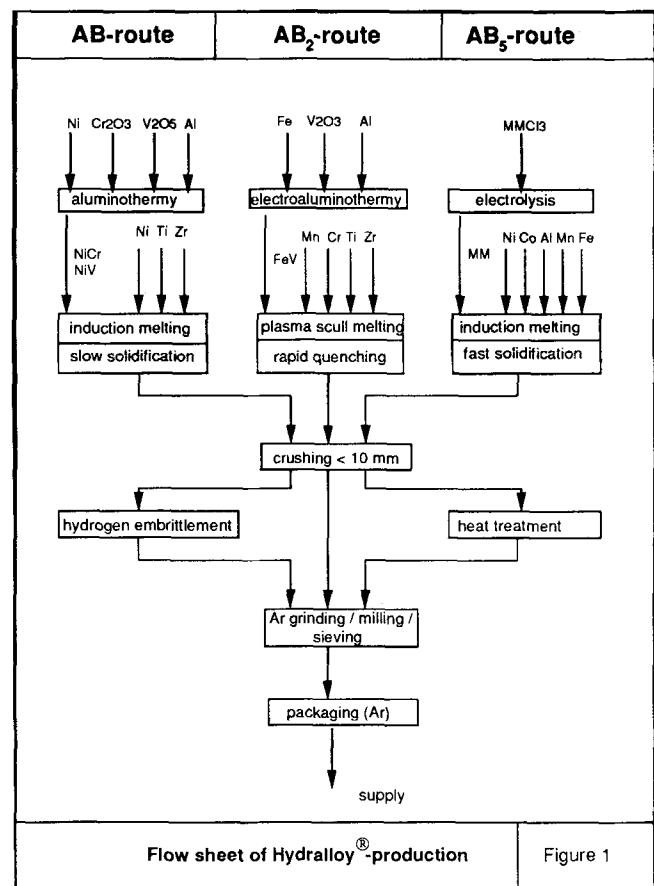
Since the end of the 1970s, hydrogen storage alloys have represented an important component of development work at GfE Gesellschaft für Elektrometallurgie mbH (GfE). AB<sub>2</sub>-alloys for the use in stationary storage or motor vehicles have been produced up to a scale of 10 tons. On the basis of this knowledge and the investment in the required special equipment, it was possible to realize the expansion to battery alloys (AB or AB<sub>5</sub> types) with success. This article provides a metallurgical overview of the different production techniques for hydrogen storage alloys (HYDRALLOY®, GfE Gesellschaft für Elektrometallurgie mbH) and shows the success achieved with upscale development to large-scale production.

## 2. Process Flow Sheet

Figure 1 shows the main process steps for the production of hydrogen storage alloy types AB, AB<sub>2</sub>, and AB<sub>5</sub>. In addition to the main component nickel, battery alloys include reactive metals like Ti, Zr, or rare earth metals, and according to their activity in the alloy, they lead to various melting techniques (e.g., crucible materials). Demands on phase distribution and grain sizes require different solidification and subsequent consolida-

tion conditions for alloy production. Last, but not least, alloy ductility and hardness is the deciding factor in the use of technology for powder production.

The alloy has to be consequently handled under inert gas from melting to packaging, because oxidation has already begun to occur at a minimally increased temperature (e.g., in the crusher and mills), which thus leads to losses of capacity.



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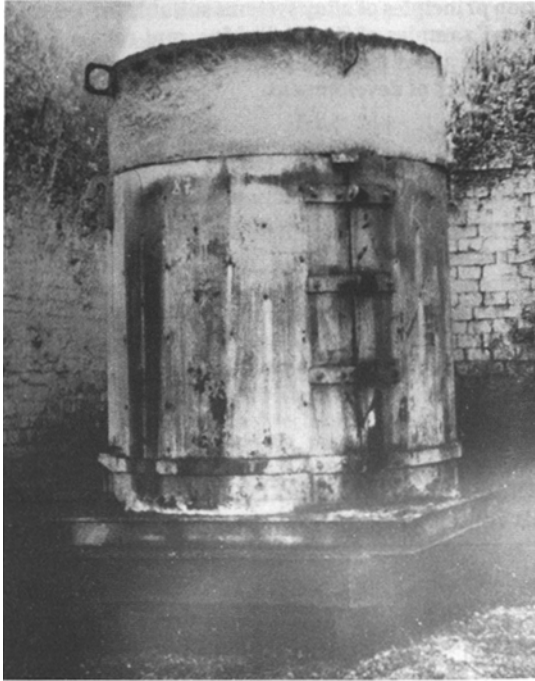
Fig. 1 Flow sheet for Hydralloy® production. Note that MM in the AB<sub>5</sub> route represents Mischmetal.

### 3. Raw Materials

GfE has a complete production line to process Hydralloy® alloys, starting with master alloys like FeV, NiCr, NiV, Cr metal, and La- or Ce-Mischmetal (battery grade). Control of unde-

sired impurities is of utmost importance. Contamination is possible by crucible reactions (e.g., Al, Si, Mg, Ca, C, S, or P), unconverted reducing agents (e.g., Al or C) and gas adsorption (O<sub>2</sub>, N<sub>2</sub>, or H<sub>2</sub>).

The production of Hydralloy with reproducible properties is possible only by precise quality assurance (production control, SPC) of internal as well as purchased raw materials. Figures 2 and 3 show production for FeV/NiCr/NiV and NiV slabs, and Fig. 4 summarizes the chemical reaction, process type, and typical composition.



**Fig. 2** Aluminothermic master alloy production of FeV, NiV, and NiCr. Size: diameter, 2000 mm; h, 2800 mm.



**Fig. 3** NiV slabs before crushing and sampling. Size: diameter, 1400 mm; h, 200 mm; w, 2t.

AB-route	AB2-route	AB5-route
$\left[\frac{1}{2} \text{Cr}_2\text{O}_3; \frac{1}{2} \text{V}_2\text{O}_5\right] + \text{Ni} + \frac{8}{3} \text{Al}$ $\rightarrow [\text{NiCr}, \text{NiV}] + \frac{4}{3} \text{Al}_2\text{O}_3$	$\frac{1}{2} \text{V}_2\text{O}_5 + \text{Fe} + \text{Al}$ $\rightarrow \text{FeV} + \frac{1}{2} \text{Al}_2\text{O}_3$	$\text{MMCl}_3 \rightarrow \text{MM} + \frac{3}{2} \text{Cl}_2$
aluminothermic	electroaluminothermic	electrolytic
<b>composition (weight-%):</b> Ni 35 ± 3; 50 ± 2 Cr 50 ± 2 or V 65 ± 3 Al 0,3 - 1	<b>composition (weight-%):</b> V 78 - 82 Fe 15 - 20 Al 0,3 - 1,8 Si 0,15 - 0,9	<b>composition (weight-%):</b> La 25 - 55    Y < 1 Ce 20 - 50    Th < 0,001 Nd 8 - 20    Fe 0,1 - 0,5 Pr 4 - 8 Gd < 1
<b>Masteralloys</b>		

**Fig. 4** Chemical reaction and product composition of master alloy production.

## 4. Melting Process

Atmospheric melting techniques are not used due to the high content of refractory metals (Ti, Zr, V, or Cr) or rare earth

metals (La, Ce, Nd, or Pr) caused by their strong oxygen affinity. Also, a critical aspect is the crucible material.  $Al_2O_3$ ,  $SiO_2$ , or carbon crucibles are excluded from use. Comprehensive and time-consuming experiments were necessary to determine optimal lining materials.

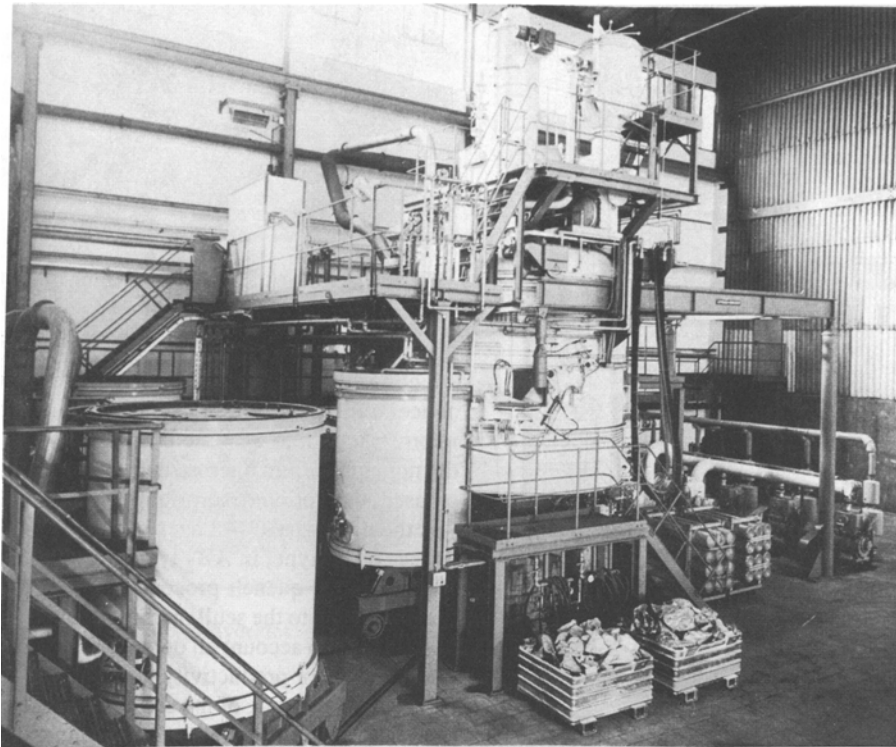
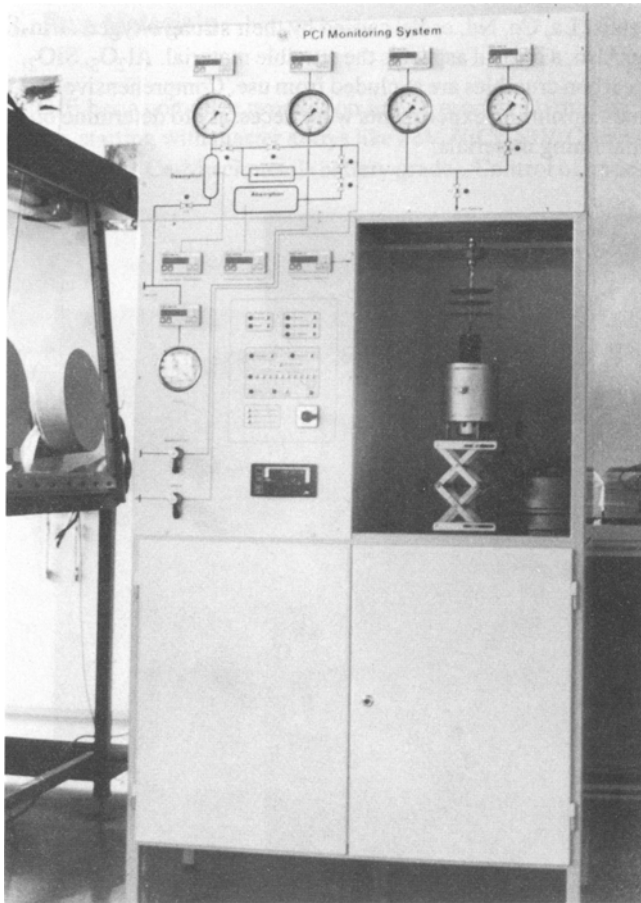


Fig. 5 Typical 1500-kg cover gas induction furnace with mobile cooling chambers.

AB-type	AB2-type	AB5-type
A: Ti, Zr, V B: Ni, Cr, V	A: Ti, Zr B: Ni, Mn, (Cr, V, Co, Fe)	A: La, Ce, Nd, (Pr, Gd, Y) B: Ni, Co, (Al, Mn, Fe)
<u>composition (range) [%]</u>	<u>composition (range) [%]</u>	<u>composition (range) [%]</u>
Zr: max. 28    Ni: max. 38 Ti: max. 18    Co: max. 7 V: max. 20    Al: max. 4 Cr: max. 9    Mn: max. 4	Ti: max. 30    Fe: max. 4 Zr: max. 30    Cr: max. 10 V: max. 14    Mn: max. 60 Ni: max. 60	MM: max. 34 Ni: max. 60 Co: max. 10 Mn + Al: max. 7
<u>metallurgical aspects:</u> high Zr-content --> no melting in oxide- ceramic crucibles. High gas content of Ni and Zr --> optimized vacuum degassing step is necessary. At least 3 different phases with specific grain size and phase distribution required --> controlled slow solidification	<u>metallurgical aspects:</u> High reactivity with crucible materials, MM-desoxidation necessary to reach oxygen-specs. Mn-losses during vacuum degassing, a two step process (FeVMn, final composition) needed to achieve good homogeneity (V-dissolution), rapidly quenching to achieve C14-Laves Phase.	<u>metallurgical aspects:</u> If carefully processed "only" conventional cover gas melting experience is necessary for melting, AB5-alloys need to be monophasic and requires a subsequent fast solidification.
<b>Cover gas metallurgy</b>		

Fig. 6 Metallurgical aspects of Hydralloy® production.



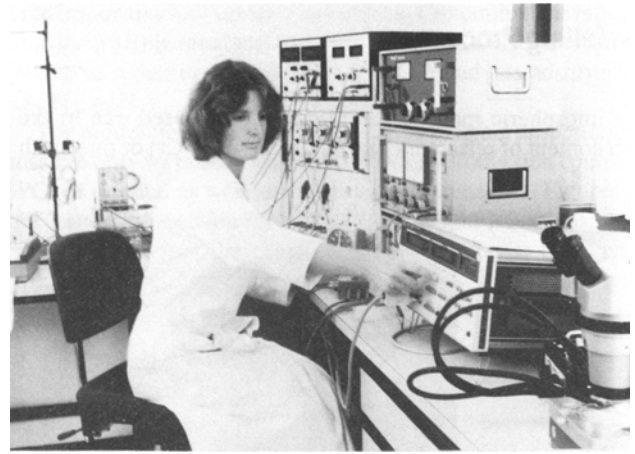
**Fig. 7** Continuous pci investigation of hydrogen storage alloys. Instrument for measuring the equilibrium hydrogen pressure in alloy samples at temperatures from room temperature to 400 °C.

For alloys with a high activity of Zr or Ti, only a crucible-free melting process is possible, which is economically feasible only in plasma-heated scull furnaces for large-scale production. With this technique, the homogenizing stirring effect of typical inductive heating is lost; consequently, the direction of the plasma flame is very important. Charging series and particle size of the different base metals are also very important. Figure 5 shows the large-scale production of Hydralloys® in induction furnaces. The largest furnace has a capacity of about 1000 tons/year and is complemented by two additional plants with half of that capacity.

Rapid analysis by sampling of the melt via X-ray fluorescence analysis (RFA) takes place before casting. This control parameter takes approximately 12 min and leads to a casting allowance (after adding grain refiners) by the quality assurance department or to a correction via additional chargement.

The different alloy types require defined crystal sizes, single- or multi-phase composition, phase ratio, and crushability, as well as different casting and solidification conditions.

Consequently, AB<sub>5</sub> alloys require slow, controlled solidification to adjust the necessary microstructures, which consists of three main phases without undesired grain growth. However, suitable AB<sub>5</sub> alloys require a single-phase microstructure,



**Fig. 8** Electrochemical characterization of battery alloy powder.

which is difficult to obtain due to the relatively small range of concentration. Ultra-rapid solidification leads, due to the fine microstructure, to extreme pyrophoricity of the powders, and the nonequilibrium microstructure (lattice stresses) leads to increased absorption/desorption pressures of hydrogen. To adjust the necessary C14 Laves phase (TiMn<sub>2</sub>-type) (C15 Laves phase, ZrCr<sub>2</sub> type, in AB<sub>2</sub>-type alloys), it is necessary to add either a rapid quench process (C14) or a controlled quench process (C15) to the scull melting process.

Taking into account all of these requirements and in consideration of plant productivity, melting and casting plants were constructed. Casting of the crucible charge can take place continuously at the optimal melting temperature. Parallel to the discharge of the cast product through a separated chamber, the next melt takes place. Figure 6 summarizes the metallurgical aspects.

## 5. Consolidation

Only for a few alloys is it possible to obtain the required properties in the cast condition. Usually, alloys are used as fine granules (<2 mm) down to powder (<45 μm), and a subsequent crushing step was possible only because of their ductility. This can be avoided by hydrogen embrittlement.

Crushing is made easier if the alloy macrostructure contains numerous cracks. Cracks are introduced by pressurization and depressurization of the alloys with hydrogen. Frequently, thermal activation is necessary to dissolve the oxide or nitride (or mixed) surface layer. Once this is done, hydrogen has free access, and its absorption takes place progressively during cooling to room temperature. The use of pure gases is obligatory.

Whereas the above-mentioned activation requires only a very low temperature treatment, many AB<sub>5</sub> alloys require high-temperature homogenization for longer times to achieve a single-phase structure. High temperatures are of interest for large-scale processing to reduce holding times. However, the possibility of the formation of undesired secondary phases increases with high temperatures. A homogeneous single-phase microstructure produces a flat, low-pressure equilibrium hydrogen pressure curve.

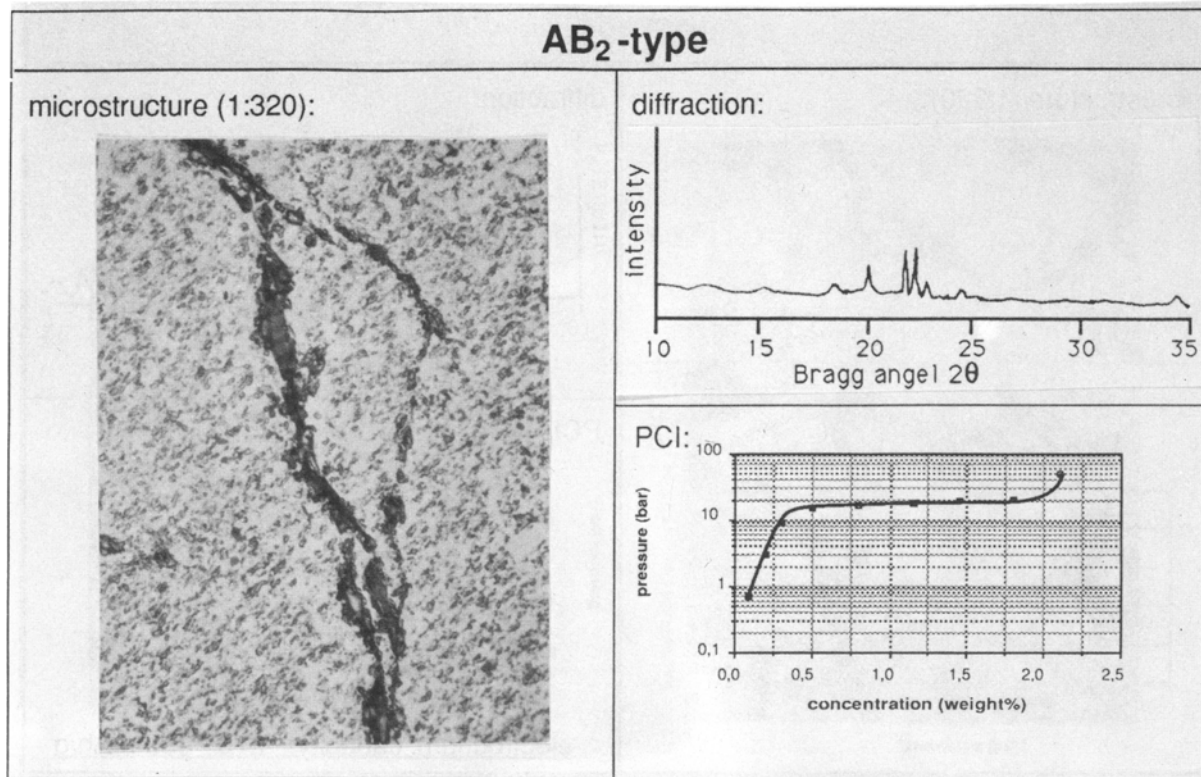


Fig. 9(a) Physical properties of AB<sub>2</sub>-type hydrides.

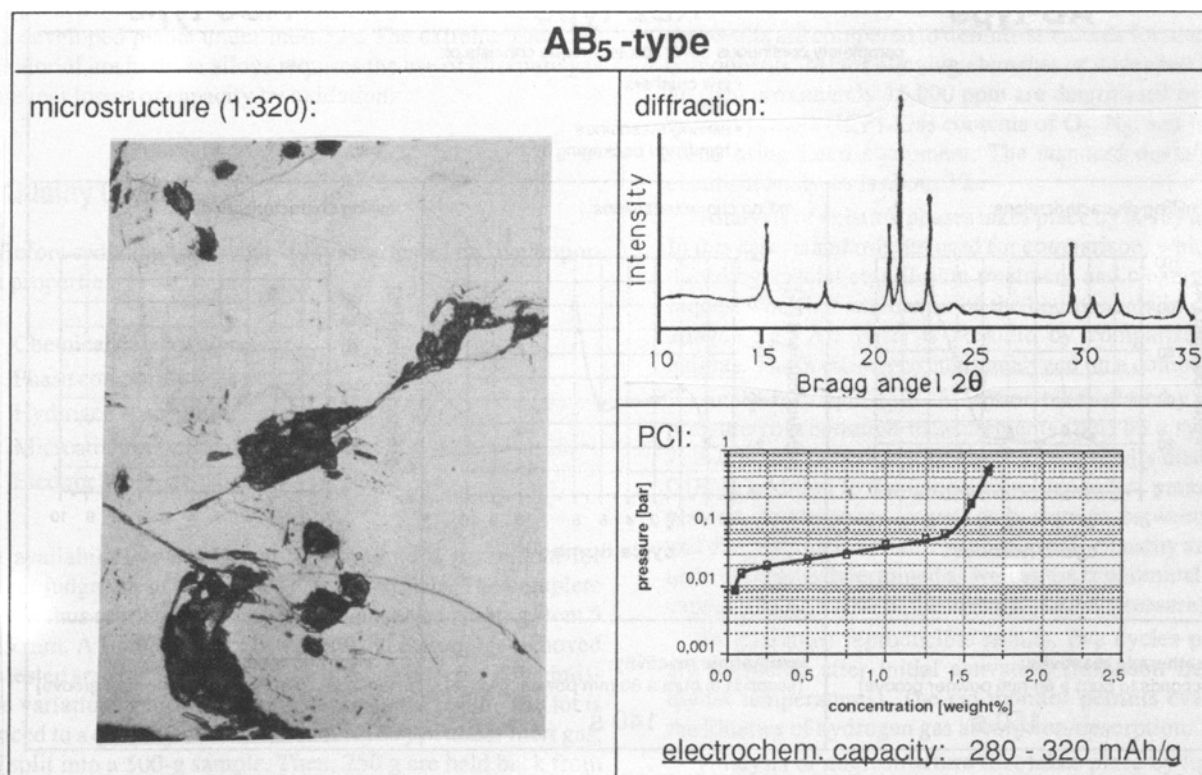
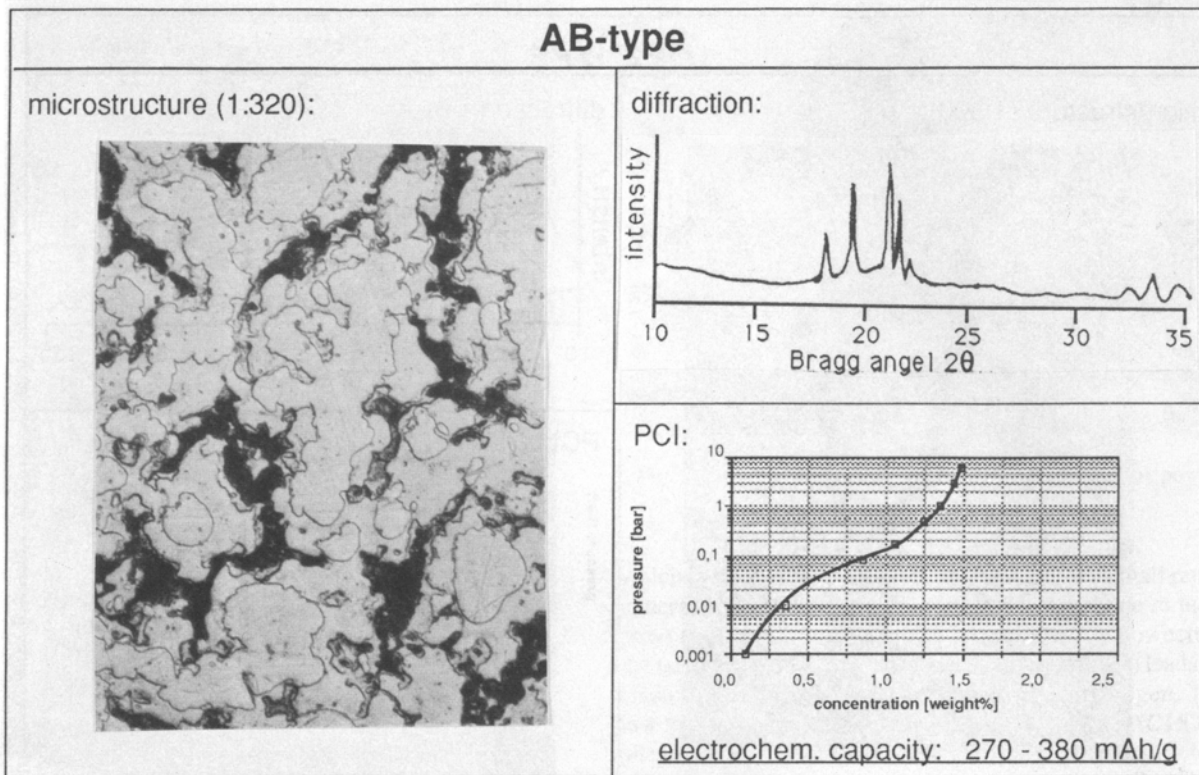
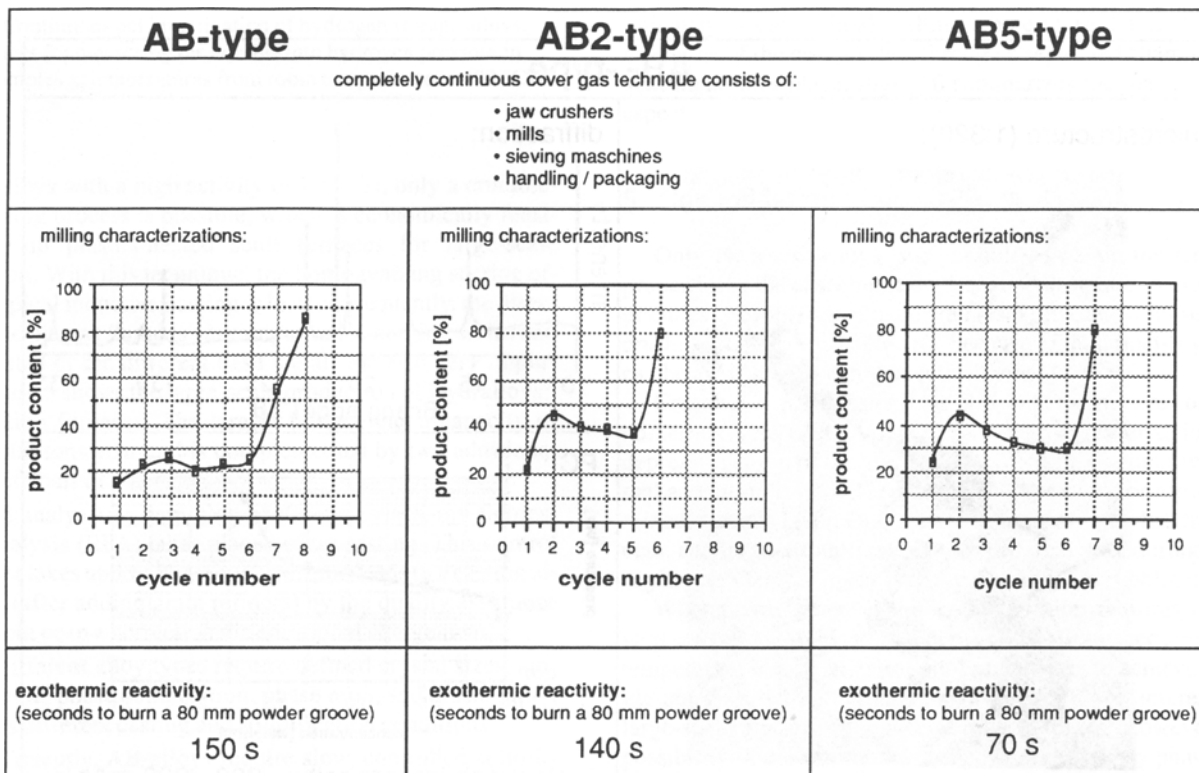


Fig. 9(b) Physical properties of AB<sub>5</sub>-type hydrides.



**Fig. 9(c)** Physical properties of AB<sub>5</sub>-type hydrides.



**Fig. 10** Milling test results for different hydride alloys (product fraction per milling cycle) and pyrophoricity tests of powders obtained by measuring burning capacity.

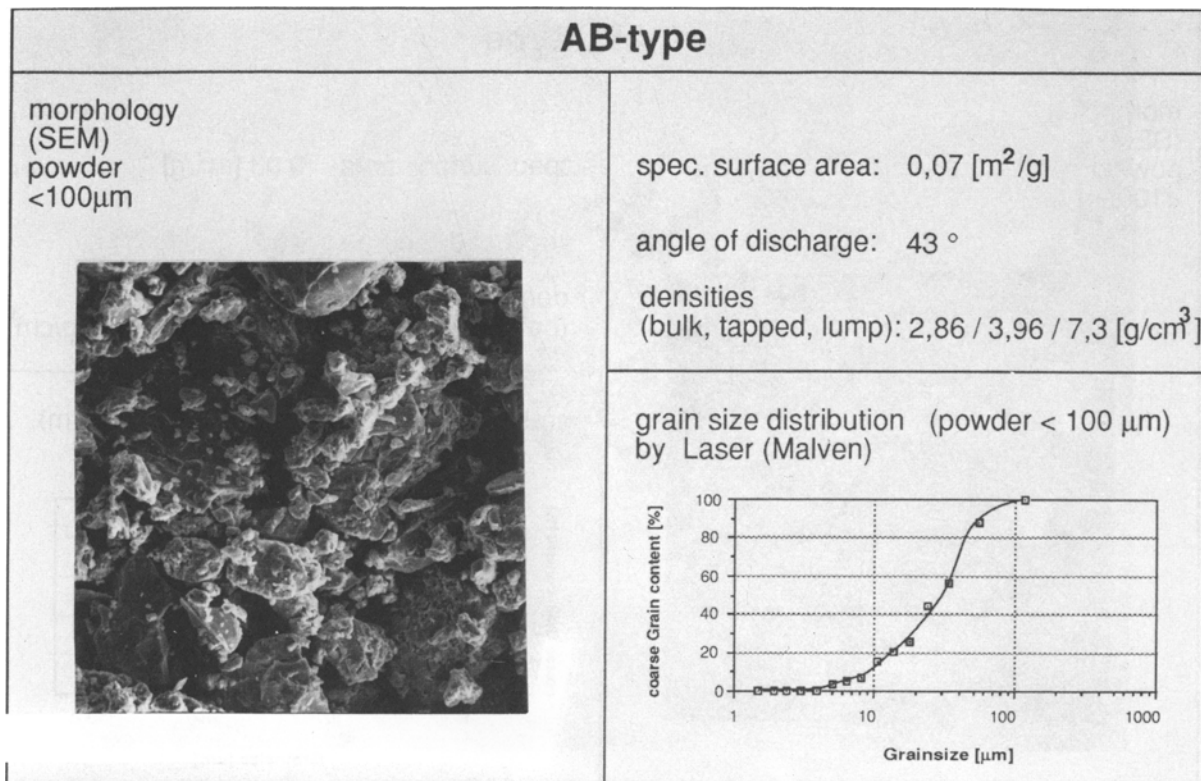


Fig. 11(a) Powder characterization of AB-type alloys.

Rapid cooling is needed to preserve the AB<sub>2</sub> microstructure, an approach that is only successful at charges of >500 kg in specific developed plants under inert gas. The extreme gettering behavior of hot hydride alloys requires the use of ultrapure gas to prevent losses of capacity by oxidation.

## 6. Quality Control

Before reducing to powder, alloys are tested on five important properties:

- Chemical composition
- Phase composition
- Hydrogen absorption
- Microstructure/microhomogeneity
- Electrochemical capacity

The availability of a representative sample is paramount for correct judgment of the consolidated materials. The complete ingot is thus crushed under argon to a grain size ranging from 5 to 25 mm. A small quantity of undersized material is removed and tested separately. This fraction must be rejected if inadmissible variations, particularly of gas constants, result. The lot is reduced to a quantity of 1%, milled to <100  $\mu$ m under inert gas, and split into a 500-g sample. Then, 250 g are held back from production as a back-up sample; the other 250 g are distributed in portions to different laboratories.

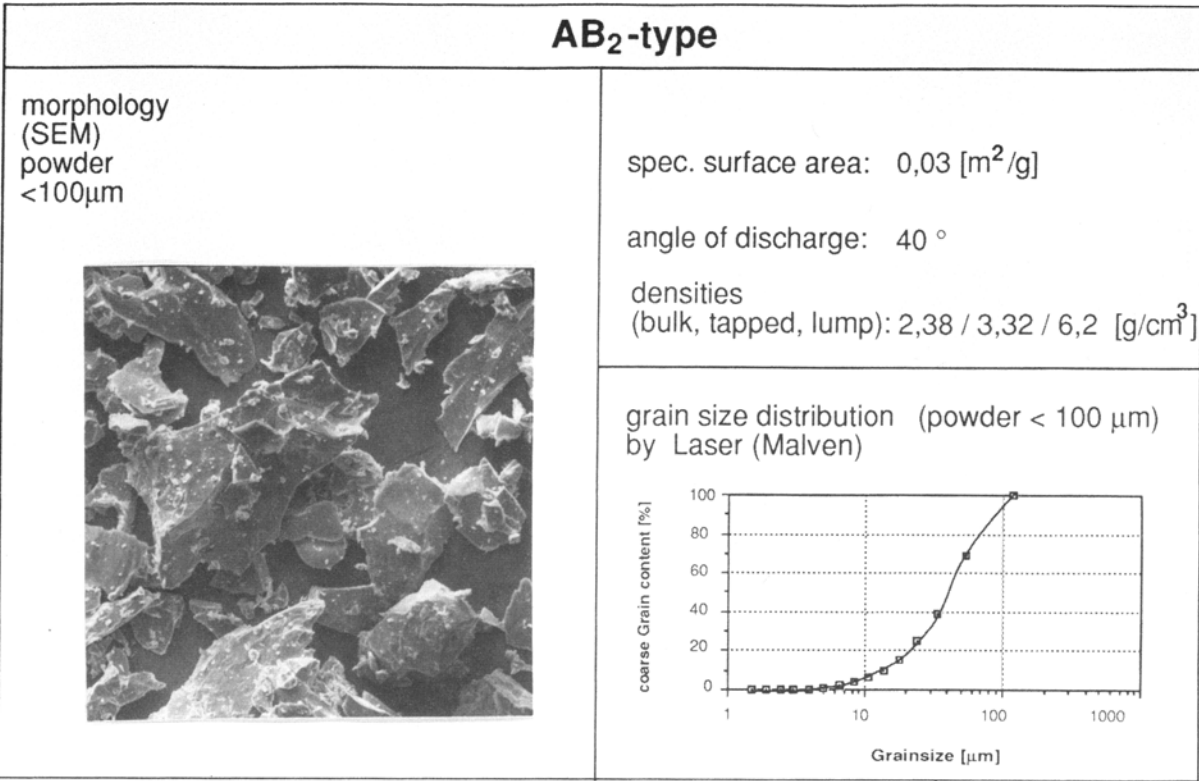
Analysis of chemical composition of the representative samples takes place by X-ray fluorescence analysis (RFA), and the results are compared to definite standards for metallic alloy components. Minor alloying elements or undesired impurities up to approximately 10,000 ppm are determined by inductive current plasma (ICP). Gas contents of O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub> are analyzed using Leco equipment. The standard deviation in the chemical analyses is about 3%.

Analysis of existing phases takes place by X-ray diffraction. In this case, standards are used for comparison, which are produced by special equilibrium treatment and clean-room techniques. The first evaluation of the components in multiphase alloys (e.g., AB type) is possible by comparison of peak heights. The X-ray spectrum is analyzed on a computer.

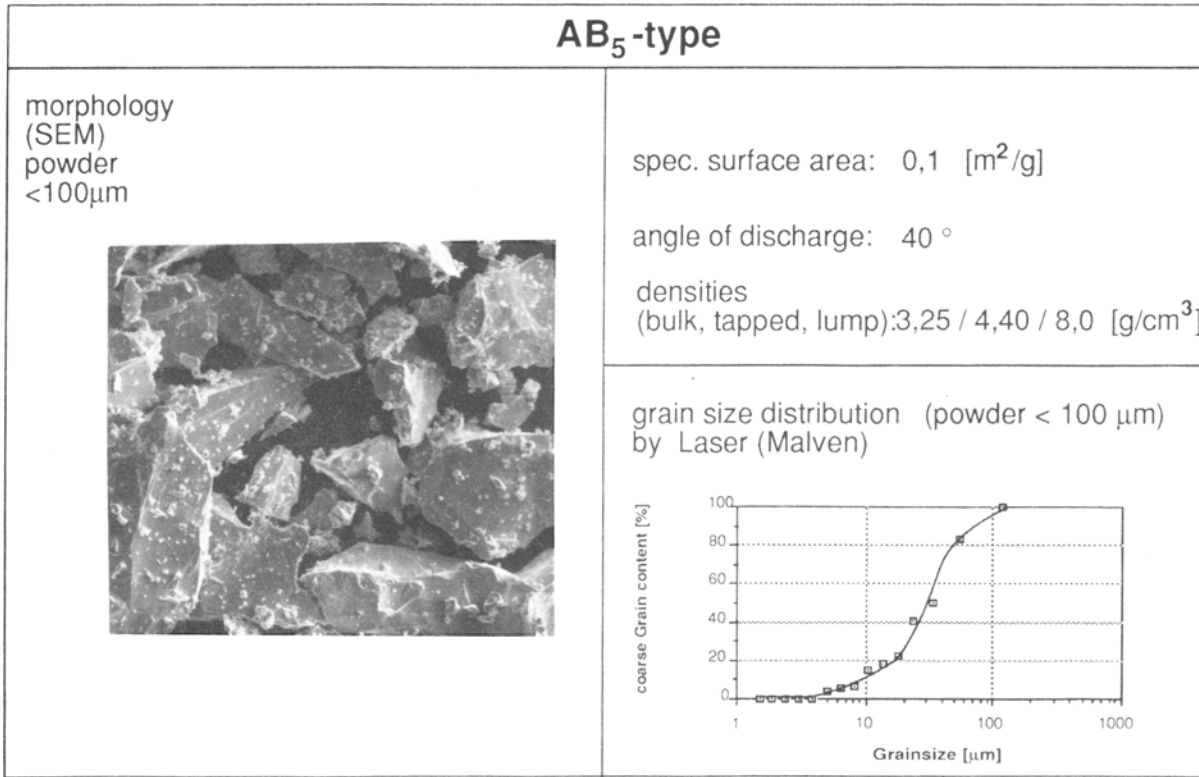
Analysis of hydrogen absorption takes place by isothermal pressure/concentration measurements (pci) on a system (Fig. 7) that is specially developed and commercially distributed by GfE. In addition to the temperature-dependent pressure of the plateau, its steepness as well as hystereses between charging and discharging is noted. The absolute H<sub>2</sub> capacity at pressures up to 100 bar is determined as well as the economical usable H<sub>2</sub> capacity (e.g.,  $\pm 10\%$  of the average plateau pressure).

To guarantee reproducible results, five cycles per sample are measured after initial activation (diffusion treatment at higher temperatures). The pci monitor permits evaluation of the kinetics of hydrogen gas absorption/desorption.

Analysis of microstructure first takes place by light microscopic inspection of polished and etched grindings. The crystal size distribution and microcracking is shown. Criteria for



**Fig. 11(b)** Powder characterization of AB<sub>2</sub>-type alloys.



**Fig. 11(c)** Powder characterization of AB<sub>5</sub>-type alloys.





**Fig. 12** Various sizes of Hydralloy®.

analysis include homogeneity and the occurrence of undesirable phases (precipitations).

Analysis of microhomogeneity takes place via SEM/EDX by quantitative analyses of single crystallites (edge/center variance). For an  $AB_5$  alloy, the value of 5 must be found to be from 4.8 to 5.2.

In the case of use as electrode materials in rechargeable batteries, analysis of the electrochemical field also takes place. For this application, samples are milled in the laboratory, mixed with conducting and binding agents, and pressed into tablets. In an electric conducting specimen holder, three cycles are conducted in KOH electrolytes with a nickel counterelectrode, and the electrochemical potential is registered against a mercury reference electrode. The charge and discharge takes place at a stable current under standardized and customer-specific parameters (Fig. 8).

Figures 9(a-c) show the three important groups of hydride alloys and provides examples of quality assurance protocols.

## 7. Powder Production

All hydride alloys are more or less pyrophoric, and therefore, all treatments on powders with a grain size below 5 mm must be done under inert gas. Treatment includes fine crushing to 0.5 to 2 mm, milling to powders down to  $<45 \mu\text{m}$ , packaging according to customer specifications in barrels, and storage of all intermediate and end products. This requires a completely closed production line and control and use of adequate pure in-

ert gas. Figure 10 shows the different millability of alloy types. In a laboratory inert gas mill, 100 g of alloy ( $<20 \text{ mm}$ ) are milled for 1 min. The product content ( $<100 \mu\text{m}$ ) is separated and replaced each cycle with fresh material. This procedure is repeated until 300 g of alloy powder is produced. Whereas the brittleness of  $AB_2$  and  $AB_5$  is approximately comparable, milling of AB alloys requires an additional expense. In opposition to this, the lower reactivity with atmospheric oxygen is exhibited by AB and  $AB_2$  alloys, which allows use of short exposure time in air without creating problems for the end user (e.g., battery producer). However, more caution is required for  $AB_5$  alloys.

An important criterion is the selection of the milling aggregate to guarantee the definite grain distribution. Some special continuous running mills produce a narrow grain band with Gaussian distribution, but for the production plant, they are very cost-intensive and inflexible. Use of a gas circuit with intermediate removal of gas impurities and fine flue dust is essential to decrease operating costs. However, the grain distribution is wider and includes all fines. A bell-shaped curve is hardly possible. However, there are enough possibilities to meet the requested specifications by varying charging speed, speed of grinding element, and charging grain sizes.

Pyrophoricity is measured in an empirical test in which the burning time needed to consume a groove (80-mm length) filled with powder is recorded. Figure 10 illustrates the pyrophoricity of Hydralloy® powders. Although AB and  $AB_2$  are mildly pyrophoric,  $AB_5$  burns within 70 s. This has to be considered during all powder handling procedures.

## 8. Quality Control

Specimens are regularly taken from the product overflow of screening machines and mixed with representative sample from the production charge. First, analysis of the grain size distribution takes place by a laser analyzer; subsequently, analyses of different density values, angle of discharge, and specific surfaces take place. Subsequently, analysis of the morphology (particle shape) is undertaken by SEM, and gaseous contamination is analyzed during the milling process by Leco analyzers. The results are summarized in Fig. 11(a-c), which show the main grain distributions that typically result after screening. The  $d_{90}$  values are situated at approximately 70  $\mu\text{m}$ , the  $d_{50}$  values at 30 to 40  $\mu\text{m}$ , and the  $d_{10}$  values at 8 to 10  $\mu\text{m}$ . Irregular-edged structures with specific surfaces exist between 0.01 and 0.07  $\text{m}^2/\text{g}$ .

In the following, the increase in oxygen content from casting to powder production is shown for an  $\text{AB}_5$  alloy, which can be achieved in large-scale production only by the use of completely closed handling:

	Ingot	Consolidated material, <20 mm	Powder, <100 $\mu\text{m}$
$\text{AB}_5$	500 $\pm$ 200	700 $\pm$ 200	1500 $\pm$ 300

In partially open systems (e.g., transfers), it is possible to achieve more than twice these amounts. Only after the analyses are completed, bins or drums are filled from the main container, and the lot is dispatched, including a certificate of analyses (ISO 9002). Examples of different grain sizes are shown in Fig. 12.

## 9. Summary

GfE's Hydride Technology Division, with activities in hydrogen storage alloys, reaction bed systems, and highly specialized electrode powders for use in the newest generation of rechargeable batteries (nickel hydride) define production aspects starting from raw materials, followed by melting, consolidation, and powderizing. The interaction of quality control and assurance to the production and resulting properties of various hydride alloys ( $\text{AB}$ ,  $\text{AB}_2$ , and  $\text{AB}_5$ ) is described. It has been shown that the specification of the battery customer can be met only by specially developed production techniques and full inert gas lines, and by establishing many control points and the use of a continuous technical support from experienced staff. The scale up from technical development to production scale was successfully realized, and powder lots in ton scales were delivered.