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CRYSTALLIZATION BEHAVIOUR OF RAPIDLY QUENCHED AND MECHANICALLY ALLOYED AMORPHOUS MATERIALS

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Amorphous metallic alloys were synthesized by the methods of rapid quenching and by mechanical alloying. In contrast to rapid quenching, mechanical alloying is a new process in producing amorphous alloys. In this paper we will report the amorphization of Ti-Cu, Hf-Cu, Hf-Ni and Fe-Ni-B alloys. The crystallization behaviour of these amorphous alloys was examined by DTA measurements with different heating rates in the range from 1 to 80 K / min. The data of mechanically alloyed powders will be compared with those of rapidly quenched materials. Further characterizations were done by X-ray diffraction, SEM and EDAX analyses. In general, the examined amorphous materials prepared by mechanical alloying or rapid quenching show very similar properties.

Introduction

Amorphous metallic alloys have been prepared for the first time by Buckel and Hilsch [1] using vapour condensation. This work stimulated the search for other amorphous alloys and for new preparation methods. Duvez et.at. [2] synthesized a few years later amorphous alloys by rapid quenching of the melt. This technique based on the necessity of a fast heat transfer leads to thin splats or ribbons depending on the performed process. The most common processes are splat-cooling and melt-spinning. Both are applied in research for synthesizing new materials and the second one is also used for industrial production of amorphous alloys.

Mechanical alloying was recently developed as a new technique to synthesize amorphous materials. This method works in contrast to the rapid quenching techniques at ambient temperatures in the solid state and converts crystalline powder mixtures to fine amorphous powders [3,4] by high energy ball milling.

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This new mechanical alloying process can be seen as a development of the milling technique used by Benjamin [5] to form supersaturated crystalline alloys and is related to the earlier fact that cold working at liquid helium temperatures can lead to the alloying of two metals [6].

In the last years a large number of amorphous alloys was prepared by mechanical alloying [7,8] but only less is known about the path of amorphization and the crystallization behaviour of these powders. Our thermoanalytical studies were carried out with respect to comparison of amorphous foils and powders and to consolidation of these materials.

Experimental

Amorphous alloys by rapid quenching

Splat-cooling and melt-spinning were employed for the synthesis of rapidly quenched amorphous alloys. For both techniques prealloyed materials were used. This starting materials were prepared from powders with a purity of at least 99.9 at. % and a particle size ranging from 60 to 125 µm. Powder mixtures of appropriate composition were well mixed, pressed and molten in an arc-furnace under purified Ar-atmosphere in a cold crucible. These master alloys were homogenized by remelting for several times and then crushed for rapid quenching. Splat-cooling was employed for preliminary tests of the amorphization behaviour of an alloy or if only small amounts were required. The splat-cooling process was performed in high vacuum or under purified Argon. The small samples were molten crucible free using rf-levitation-melting. The molten droplets were then squeezed and quenched between two polished copper pistons. By this technique amorphous alloys were prepared of different Hf-Ni, Hf-Cu and Ti-Cu alloys. The splats were about 30 - 40 µm thick with diameters ranging from 20 to 30 mm.

As an alternative method melt-spinning was used to produce larger quantities of rapidly quenched amorphous materials. The process was carried out with a specially developed melt-spinning equipment for operation in high vacuum shown in Fig. 1. In this equipment the alloy is molten in cold or warm crucibles by rf-heating. The melt is ejected by gas pressure through a fine nozzle onto a fast rotating water-cooled copper wheel. The molten jet is quenched very rapidly during the heat contact with the wheel and thin ribbons are produced with a

thickness of about 30 μm. The width can be varied between 2 and 30 mm depending on the dimensions of the installed nozzles. With this system we were able to prepare amorphous ribbons of Hf-Ni, Hf-Cu, Ti-Cu and Fe-Ni-B alloys. Some of them are shown in Fig. 2.

Amorphous alloys by mechanical alloying

Fine elemental powders were used with a grain size up to 1 μm in average for the preparation of amorphous materials by mechanical alloying (MA). The purity of the elemental powders was 99.9 at % for the metals. The powders were hand mixed before loading into hardened steel vials together with the milling balls for performing the milling process to synthesize amorphous powders. The vials were sealed with O-rings and filled with dry Argon (≧99.999 %) to prevent oxidation during milling. The milling process was carried out with commercially available vibratory and rotating mills. However the milling vials were specially developed for amorphization of these alloys. Small portions of material were periodically extracted for monitoring the amorphization process. The milling

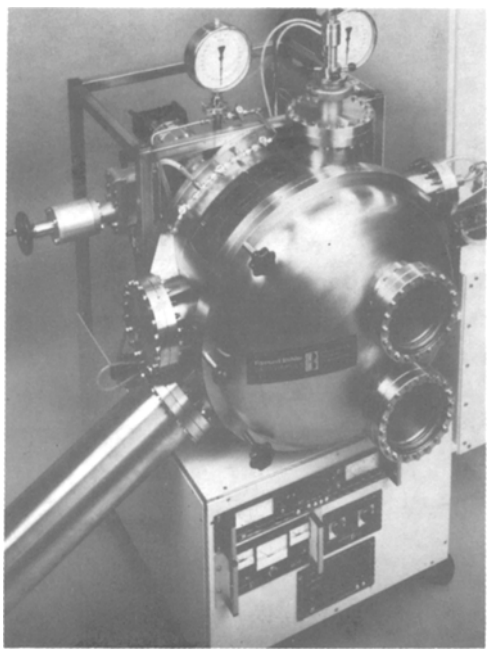

Fig. 1 Equipment for preparation of amorphous alloys by melt-spinning in high vacuum. The outer part of the crucible system with viewing port for temperature control can be seen at top of the vacuum chamber [9].

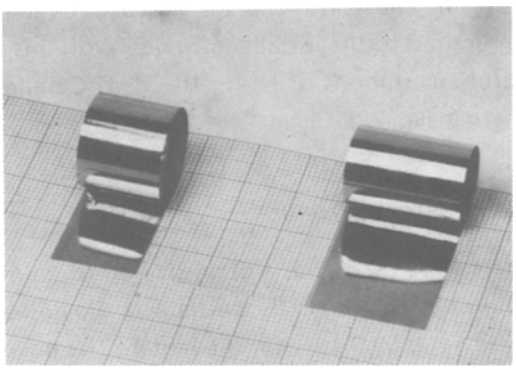

Fig. 2 Amorphous ribbons of Ni-base alloys prepared with the melt-spinning equipment.

process was stopped when no further variation of the X-ray diffraction patterns and the DTA signal could be observed. The process was carried out at ambient temperature and no significant heating of the vials during milling was detected in consequence of the used air cooling. Depending on the employed milling system charges of amorphous powders between 5 and 100 g per run could be obtained.

Characterizations

The structural analyses of the mechanically alloyed powders and the rapidly quenched materials have been done by X-ray diffraction in a diffractometer with Ni-filtered CuK_α-radiation in backscattering. The X-ray diffraction of alloyed powders was carried out on a sieved fraction with a grain size of less than 45 μm.

SEM and EDAX-analyses were employed for additional characterizations of the mechanically alloyed amorphous powders with respect to particle size, chemical composition and homogeneity.

The differential thermal analysis (DTA) studies were performed in a Netzsch apparatus type 404 S on powders (particle size less than 45 μm) or pieces of foils. The used sample mass depended on the choosen heating rate and varied between 200 mg for dT/dt = 1 K/sec and 50 mg for dT/dt ≧ 20 K/sec. As reference an equal mass of Al_2O_3 was employed. Sample and reference crucible

were of Al_2O_3. Before starting the measurements the DTA-chamber was evacuated and filled with He. The DTA-studies were conducted in a dynamic He atmosphere with a flow rate of 50 cm^3 /min.

Results

With our employed mechanical alloying method amorphous alloys could be formed in a wide range of composition for the examined binary systems of Ti-Cu, Hf-Cu and Hf-Ni. The mechanically alloyed powders show a rough surface structure, as can be seen in Fig. 3. The surface structures of the examined powders are very similar. However a dependence of particle size on composition was observed. The finest powders were obtained in the Ti-Cu system. The amorphous phase shows the widest range of homogeneity in the Ti-Cu system and extends from about 10 to 90 at % Cu [7]. The highest crystallization temperature was observed in the Hf-Ni system for the composition $Hf_{35}Ni_{65}$. Some measured crystallization temperatures are listed in Tab. 1 and compared with amorphous alloys prepared by splat-cooling or melt-spinning.

A more detailed comparison of the thermoanalytical behaviour of rapidly quenched and mechanically alloyed materials will be given in the following for Hf-Ni alloys.

The rapidly quenched amorphous Hf-Ni alloys were produced by the splat-cooling technique. The compositions and a short characterization of the detected differential thermal analysis (DTA) curves are given in Tab. 2. The first exothermic peak indicates the transformation from amorphous to crystalline state. For alloys with a higher Hf-content a more complexe crystallization behaviour was observed. Typical DTA curves are shown in Fig. 4. Amorphous Hf-Ni alloys could be formed by rapid quenching only near the composition ratios 1 : 2 and 2 : 1. The crystallization temperatures of the examined alloys are plotted as a function of the Hf-content in Fig. 5. The observed crystallization temperatures show a linear dependence on composition for both homogeneity ranges. The alloys near the composition Hf_1Ni_2 exhibit the higher crystallization temperatures.

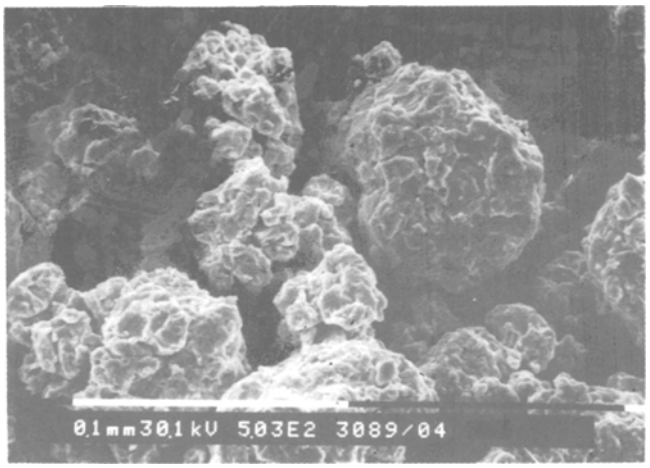

Fig. 3 Micrograph showing the shape of mechanically alloyed amorphous $Ti_{50}Cu_{50}$ material.

Comparison of MA-materials and Splats of $Hf_{35}Ni_{65}$

The composition $Hf_{35}Ni_{65}$, having the highest crystallization temperature of the amorphous Hf-Ni-splats investigated in this paper, was chosen for this comparison of rapidly quenched and mechanically alloyed amorphous materials.

The synthesized structures of both, the mechanically alloyed powders and the liquid quenched foils were first analysed using X-ray diffraction to ensure that the material produced was completely amorphous. Fig. 6 shows the X-ray patterns for both $Hf_{35}Ni_{65}$ samples. The materials show diffraction diagrams with a broad, structureless peak near 40° in 2 θ. This shape of diffraction profile indicates the presence of an amorphous phase.

Differential thermal analyses were carried out at the same samples using a heating rate of 20 K/min. The results are shown in Fig. 7. Both materials show very similar crystallization behaviours with two exothermic reaction peaks. The peak near 600° C indicates the transformation to crystallinity. This temperature depends on the heating rates and is shifted to lower temperatures for smaller heating rates. A transformation temperature of about 500° C is obtained by extrapolation to isothermal conditions.

Table 1: Crystallization temperature of amorphous Ti-Cu, Hf-Cu, Hf-Ni and Fe-Ni-B alloys obtained with a heating rate of 20 K/min (the T_c-value of dominant reaction is listed)

Composition	Preparation	T_c peak
$Ti_{40}Cu_{60}$	Splat	426,4
$Ti_{50}Cu_{50}$	Splat	408,2
$Ti_{57}Cu_{43}$	Ribbon	428,6
$Ti_{63}Cu_{37}$	Splat	417,1
$Hf_{55}Cu_{45}$	Splat	512,2
$Hf_{46}Cu_{54}$	Splat	536,8
$Hf_{36}Cu_{64}$	Splat	561,4
$Hf_{60}Ni_{40}$	Splat	540,2
$Hf_{35}Ni_{65}$	Splat	630.0
$Hf_{30}Ni_{70}$	Splat	584,0
$Ti_{45}Cu_{55}$	MA	442,0
$Ti_{50}Cu_{50}$	MA	366,0
$Ti_{57}Cu_{43}$	MA	430,0
$Hf_{60}Cu_{40}$	MA	509,1
$Hf_{50}Cu_{50}$	MA	559,6
$Hf_{30}Cu_{70}$	MA	549,7
$Hf_{35}Ni_{65}$	MA	620,7
$Hf_{35}Ni_{65}$	MA	589,7
$Hf_{50}Ni_{50}$	MA	609,8
$Fe_{40}Ni_{40}B_{20}$	Ribbon	434,4
$Fe_{40}Ni_{40}B_{20}$	Splat	439,1
$Fe_{40}Ni_{40}B_{20}$	MA	354,1

Table 2: Characterization of DTA-signals and crystallization temperatures of some Hf-Ni splats (DTA-heating rate: 20 K/min)

Composition	DTA-peak characterization	T onset (°C)	T peak (°C)
$Hf_{76}Ni_{24}$	3 peaks (double-peak and single peak)	430	450, 490, 580
$Hf_{66}Ni_{34}$	3 single peaks (first peak largest one)	490	500, 570, 650
$Hf_{60}Ni_{40}$	2 peaks of nearly same size	530	540, 590
$Hf_{35}Ni_{65}$	2 peaks (first peak dominant)	600	630, 760
$Hf_{30}Ni_{70}$	2 peaks (first peak dominant)	570	580, 740

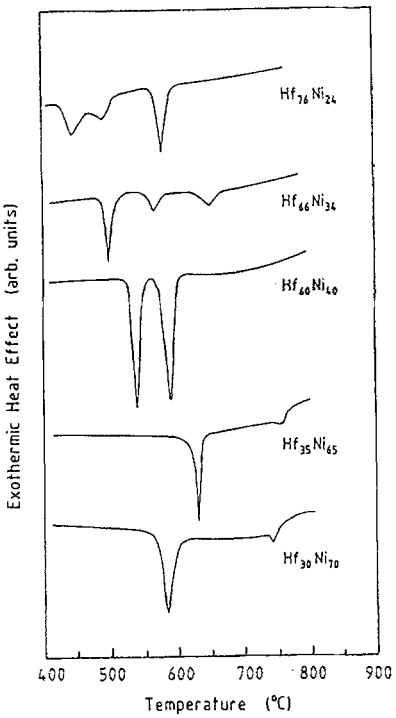

Fig. 4 DTA-curves of rapidly quenched amorphous Hf-Ni alloys. The heating rate was 20 K/min. The highest crystallization temperature was measured for the composition $Hf_{35}Ni_{65}$.

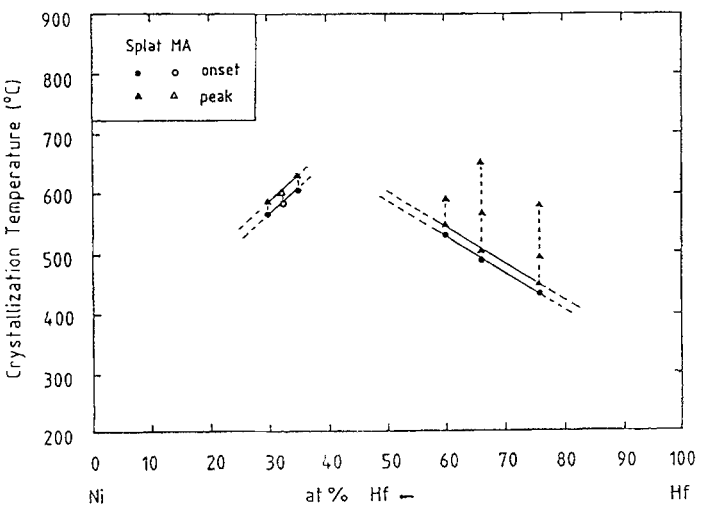

Fig. 5 Crystallization temperature as function of the Hf-content. The measurements were carried out at a heating rate of 20 K/min.

The activation energies of this crystallization processes were studied by doing a series of DTA-runs with different heating rates. For this determination heating rates of 1, 5, 10, 20, 40 and 80 K/min were used. These measurements show a small difference for the observed crystallization temperatures. The slightly lower peak position of the MA-material might be caused by a deviation from the nominal composition; correction done by using Fig. 5 leads to an actual composition of about $Hf_{33}Ni_{67}$.

The observed dependence of the crystallization temperatures on heating rates (α) was used for the experimental determination of the activation energies by the peak-shift method [10]. The kinetics of the crystallization reaction can be determined by plotting α/T^2_{cryst} vs $1/T_{cryst}$. This Arrhenius type plot is described by the following equation:

$$- \ln (\alpha/T^2_{cryst}) = (E_a/R)\,(1/T_{cryst}) + \text{const.}$$

If the crystallization process is governed by a single activation process, these plots become a straight line and the slope of the line being proportional to E_a. The diagrams and the results for the $Hf_{35}Ni_{65}$-materials are shown in Fig 10 and 11. The activation energies are determined for the DTA-peak maximum temperature, being the more accurate value, and for the peak onset temperature. For the $Hf_{35}Ni_{65}$ splat an activation energy was calculated to E_a = 509 kJ/mol resp. 5.28 eV for the onset temperature and to E_a = 508.7 kJ/mol resp. 5.27 eV for the peak maximum temperature.

For the examined MA-material the difference between the two E_a-values is greater, in consequence of a more difficult determination of accurate onset temperature. The values calculated are E_a = 412.5 kJ/mol resp. 4.3 eV for the onset temperatures and E_a = 359 kJ/mol resp. 3.7 eV for the peak maximum temperatures. The crystallization of the examined MA-material starts easier than the crystallization of the rapidly quenched material.

Conclusions

Amorphous materials can be prepared by mechanical alloying and liquid quenching. Sometimes mechanical alloying produces amorphous materials within a much wider range of composition than liquid quenching (e. g. Ti-Cu system).

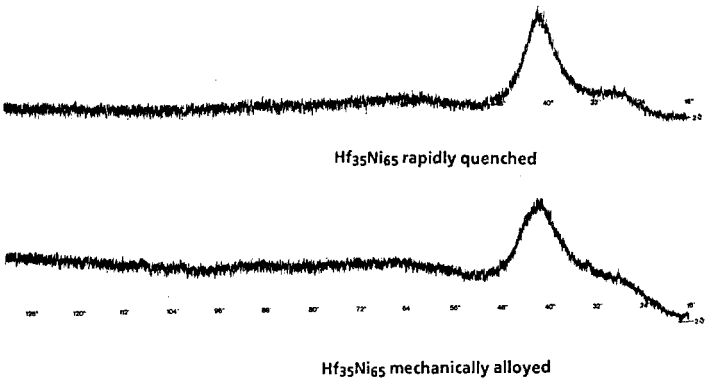

Fig. 6 X-ray diagrams of a $Hf_{35}Ni_{65}$ alloy prepared by liquid quenching and mechanical alloying.

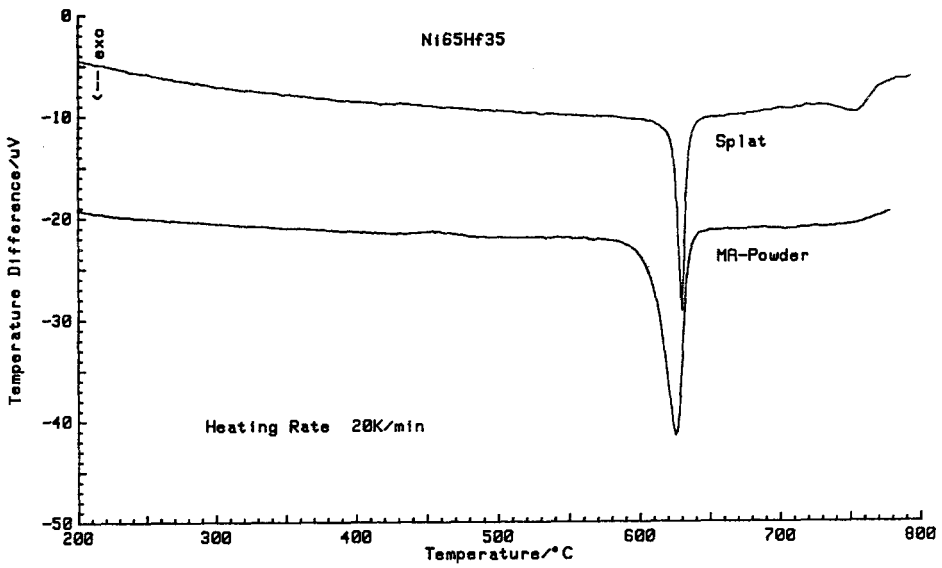

Fig. 7 DTA-curves of a liquid quenched (Splat) and mechanically alloyed (MA-powder) Hf_{35} Ni_{65} alloy.

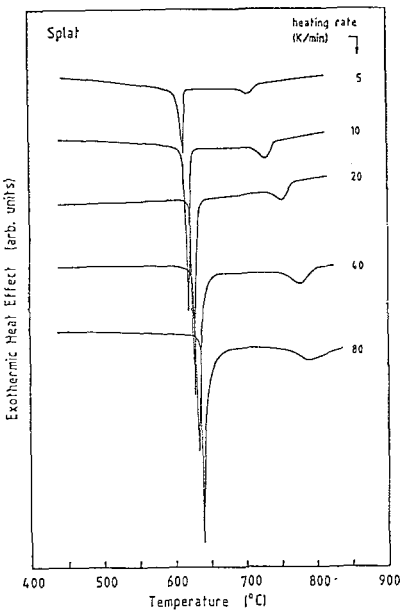

Fig. 8 DTA-scans of $Hf_{35}Ni_{65}$ splats obtained by different heating rates

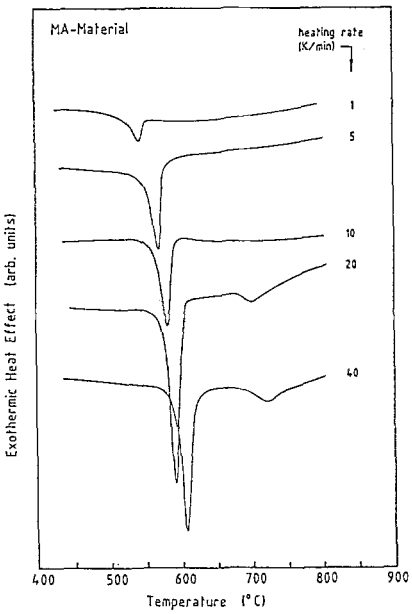

Fig. 9 DTA-scans of $Hf_{35}Ni_{65}$ mechanically alloyed, obtained by different heating rates.

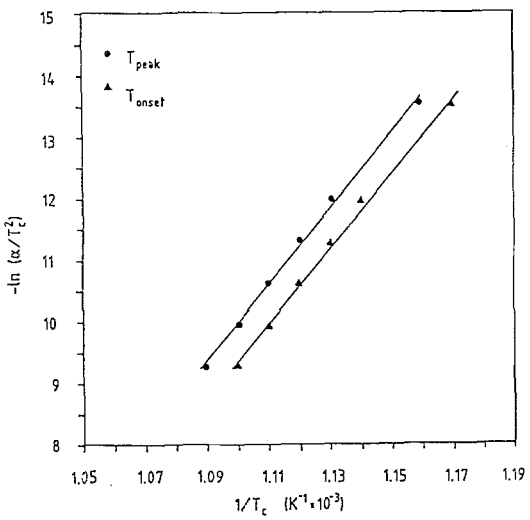

Fig. 10 Kissinger plot of liquid quenched $Hf_{35}Ni_{65}$ for determinining the activation energie E_a.

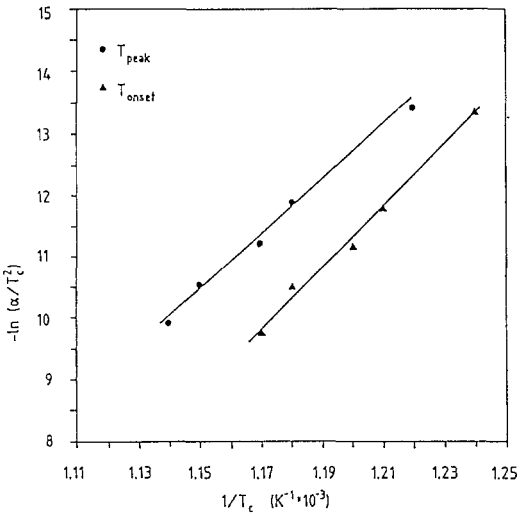

Fig. 11 Kissinger plot of mechanically alloyed $Hf_{35}Ni_{65}$ for determining the activation energie E_a.

X-ray analyses and DTA-measurements showed, that MA and LQ materials exhibit very similar properties. The observed small differences in activation energies may be caused by deviations of the composition and should not be related to the preparation process.

This thermoanalytical investigations were carried out with respect to consolidation of these amorphous materials. We used them also for extrapolating crystallization temperatures to isothermal conditions as required for doing warm consolidation [10]. However, structural changes were detected below this extrapolated crystallization temperature during annealing. This reactions were enlarged by warm consolidation[10]. It seems that the crystallization behaviour of amorphous powders is much more complex than can be seen from the DTA-analyses.

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Amorphe metallische Legierungen wurden sowohl durch Anwendung der Schnellabschreckverfahren Splat-Cooling und Melt-Spinning als auch durch mechanisches Legieren hergestellt. Im Gegensatz zu den Schnellabschreck-verfahren handelt es sich beim mechanischen Legieren um einen Prozeß zur Synthese amorpher Materialien, der erst seit einigen Jahren bekannt ist. Wir berichten in dieser Arbeit über den Einsatz dieses neuen Verfahrens zur Amorphisierung von Ti-Cu, Hf-Cu, Hf-Ni und Fe-Ni-B Legierungen und vergleichen diese mit schnell abgeschreckten Materialien. Die Charakterisierung der Proben erfolgte mittels Röntgenbeugung. Differential-Thermo-Analyse (DTA) und Elektronenmikroskopie (SEM und EDAX). Das Kristallisationsverhalten der amorphen Legierungen wurde unter Anwendung von Aufheizgeschwindigkeiten zwischen 1 und 80 K/min untersucht. Diese heizratenabhängigen Messungen wurden sowohl zur Bestimmung von Aktivierungsenergien als auch zur Extrapolation von Kristallisationstemperaturen für isotherme Bedingungen verwendet, wie sie bei der Kompaktierung amorpher Materialien auftreten. Die durchgeführten Untersuchungen zeigten, daß schnell abgeschreckte und mechanisch legierte amorphe Materialien sehr ähnliche Eigenschaften aufweisen.

Резюме – Методами быстрого охлаждения и механического сплавления получены аморфные металлические сплавы. По сравнению с методом быстрого охлаждения, механическое сплавление представляет новый процесс в получении аморфных сплавов. Описана аморфизация сплавов Ti-Cu , Hf-Cu , Hf-Ni и Fe-Ni-B.

Кристаллизация сплавов была изучена методом ДТА при скоростях нагрева от 1 до 80 К/мин. Данные для механически сплавленных порошков сопоставлены с данными для быстро охлажденных сплавов. Дальнейшая характеристика сплавов была проведена рентгенографическим методом и методом SEM и EDAX . Сделано заключение, что аморфные материалы, полученные механическим сплавлением или быстрым охлаждением, показывают очень подобные свойства.