MECHANICAL ALLOYING OF TI-NI BASED MATERIALS USING THE SIMOLOYER®

(*Zoz - horizontal rotary ball mill*)

H. Zoz[1], D. Ernst[2], I. S. Ahn[3], W.H. Kwon[4]

[1]Zoz GmbH, D-57482 Wenden, Germany. [2]University of Siegen, D-57068 Siegen, Germany.
[3]Gyeonsang National University, Chinju, Gyeongnam, 660-701 Korea
[4]Korea Advanced Materials Institute, Seoul, 152 - 059 Korea

Abstract

The production of large quantities of contamination free mechanically alloyed powders from titanium and nickel based materials has proven to be major challenge. Feasibility of such a goal can be carried out, at laboratory level, by any milling device like the very common planetary ball mill. In this case however, the possibility of a subsequent scaling up for larger production is hindered by the intrinsic limits of a planetary ball mill design. On the contrary the Simoloyer (Zoz - horizontal rotary ball mill) can be experimented at laboratory level using small volume chamber-units (0.25, 0.5, and 2 l) and, for industrial production, using the large volume units (up to 400 l) based on the same conceptual design. Therefore, experiments have been conducted on blended elemental Ti-Ni compositions in the proportion Ti-50Ni, Ti-49.5Ni and Ti-48.5Ni (at%) using a Simoloyer with a small unit-chamber (0.5 l). Due to the inherent ductility of the powder, the material has the tendency to adhere to the grinding unit and the grinding media. Further, in order to avoid high contamination and to make the process realistic from an economical point of view, the milling time has to be reduced to a minimum. The above points identify a Critical Milling Behavior (CMB) of the system under investigation that must be kept under control to achieve the wanted goal. It will be shown by the present paper that by adopting a suitable milling and discharging procedure (Cycle Operation by Operation Cycle and Discharging Cycle) the milling effect and a good yield have been substantially achieved. This is investigated by scanning electron microscopy and X-ray diffraction.

1. Introduction

During the last years the mechanical alloying technique [1, 2] has been found to be very effective in producing powders with interesting properties. By this means it is possible to synthesize alloys or composite materials with highly dispersed components far away from thermal equilibrium state like amorphous or nanocrystalline materials. Furthermore, the powder route is a way to combine elemental or prealloyed components to materials which are generally not receivable by conventional processing techniques due to e.g. the immiscibility of their components [4].

In most cases mechanical alloying leads to material transformation of the crystalline structure by solid state reactions. The Gibbs´ free energy is increased to higher levels during milling and results in reactions of a lower metastable or stable state. The interaction between milling balls and powder particles can be characterized by processes like cold-welding, plastic deformation and further fragmentation of the particles. Atomic dislocations, a high defect structure of the lattice, the immense magnification of the boundary surface and a high diffusion rate leads to low activation energies for those reactions [5].

The powders which are usually processed consist of components with different material properties. Often a ductile powder component is combined with a brittle component. In the first stage of the milling process the ductile particles are plastically deformed. The surfaces of the harder particles are covered and enclosed by the ductile component. In most cases this milling sequence is critical due to the inherent adhesion tendency of the powder sticking to the grinding unit and the steel balls. A lot of alloying systems identify such a Critical Milling Behavior (CMB) [6]. To reduce the possibility of powder contamination caused by abrasive wear of the component parts of the Simoloyer and the balls, long milling intervals have to be avoided. Therefore, the alloying process should be carried out at a maximum efficiency in a short time interval especially with respect to the economical point of view in later industrial applications. Taking into account that a scaling up for larger powder productions in a planetary ball mill is hindered by the intrinsic limits of this milling device, on the contrary the Simoloyer is a suitable device. Based on the same conceptual design the production of powders for laboratory applications becomes possible as well as for industrial applications using small volume chamber-units (0.25, 0.5 and 2 l) respectively large volume units (up to 400 l) which leads to powder charges from 50 g up to half a ton.
An example for an alloying system with CMB character is represented by the alloying system Ti-Ni which was processed in a Simoloyer for experimental investigations. The processing of powder was carried out by using Cycle Operation [6], a special operation and discharging procedure.

2. Mechanical Alloying of Ti-50Ni, Ti-49.5Ni and Ti48.5Ni (at%)

2.1 Starting Powders

The Ti-Ni starting powders were a powder blend of elemental Ti-powder and elemental Ni-powder. The starting powders and the evolution of the milling process were investigated by a scanning electron microscope (SEM) *Cambridge CamScan 24*. The X-ray diffraction patterns were resolved by a *Seifert PTS 3000* diffractometer (XRD) using monochromatic CuK$_\alpha$ radiation. *Fig. 1.a* and *Fig. 1.b* show the particle shape of elemental Ti and Ni starting powder.

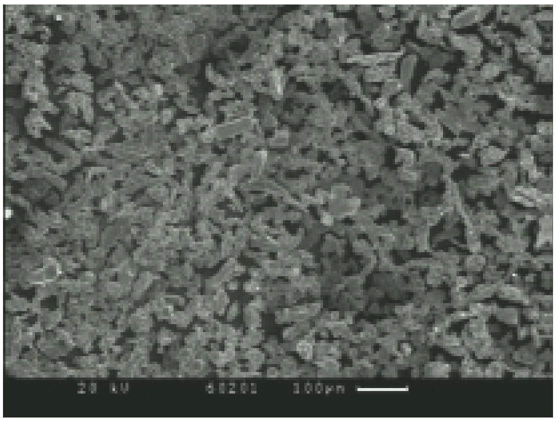

Fig. 1.a: *Ti starting powder*

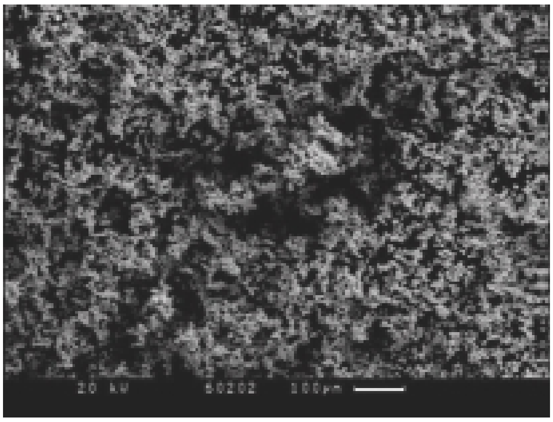

Fig. 1.b: *Ni starting powder*

It can be seen that both starting powders are characterized by broad particle size distributions. In the case of Ti the sizes vary from 40 microns up to sizes of 100 microns. The particle shape is fissured and irregular. The Ni starting powder exhibits particle sizes about 10 microns. Their geometries are of a regular shape. The X-ray diffraction pattern in *Fig. 2* proves the presence of crystalline phases.

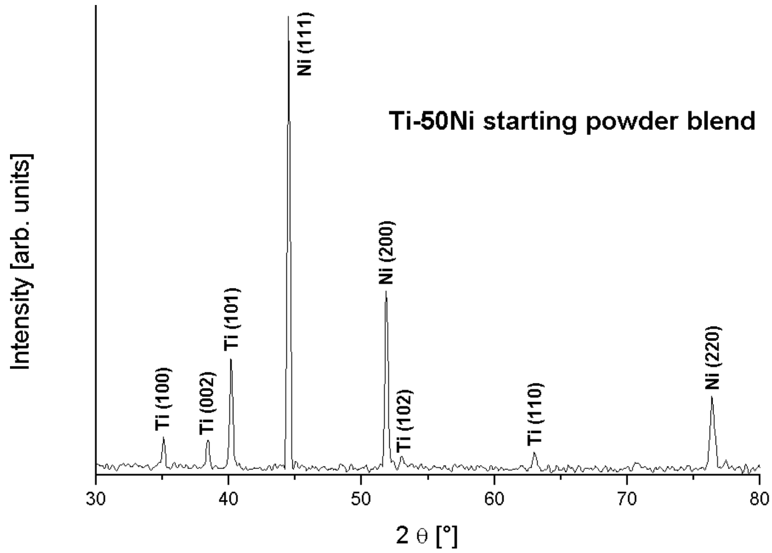

Fig. 2: *X-ray diffraction pattern of the Ti-50Ni starting powder blend*

2.2 Milling Device

The milling experiments were carried out with blended Ti-24Al-11Nb (at%) in a *Simoloyer CM01* (Zoz - horizontal rotary ball mill) with a chamber volume of 0.5 l (*Fig. 3, CM01-2l*). The principle of the Simoloyer bases on a horizontally borne rotor in a strong design which allows the transfer of a high and homogeneous kinetic energy of ball impacts. Charging, discharging and milling can be performed under defined conditions like vacuum or inert gas atmosphere. The temperature of the milling chamber unit can be controlled by a cooling system. Different chamber volumes are available from 0.25 l up to 400 l for laboratory respectively industrial application. The special design allows the scaling-up of the milling process.

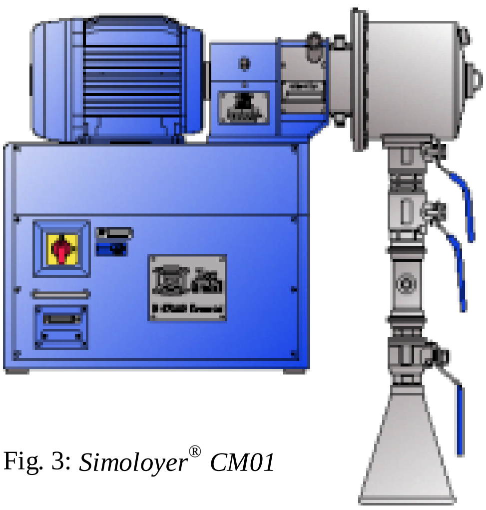

Fig. 3: *Simoloyer® CM01*

2.3 Milling Parameters

First the starting powders were premixed in the compositions of Ti-50Ni, Ti-49.5Ni and Ti-48.5Ni (at%). To avoid reactions with oxygen, the powders were handled under inert gas atmosphere (argon). Each time an amount of 100 g of premixed powder was filled into the charging container. The powder to ball weight ratio was chosen as 1:10. The used conventional steel balls (100Cr6) had an average diameter of 5.1 mm (*Table 1*). After evacuation of the milling chamber unit and refilling it with argon, the milling process was started. Several milling intervals of 1, 3, 5, 6, 7, 8, 9 and 10 hours were carried out and the resulting powders were investigated by SEM and XRD. The present paper does not describe all trials, but the important ones. Since the Ti-Ni powders show a CMB (Critical Milling

Behavior) due to their high ductility, the procedure of Cycle Operation was to be applied. Thus, being used for Operation and Discharging allowed the alloying process as well as an acceptable high powder yield (see section 3).

Simoloyer:	CM01-0.5 l with water-cooled container
Milling balls:	Material: steel (100Cr6)
	Diameter: 5.1 mm
	Total weight: 1000 g
Weight of powder charge:	100 g
Powder/ball-weight ratio:	1:10
Rotational speed:	Cycle Operation, 1500 / 900 min^{-1} , 4 / 1 min (see chapter 3.)
Milling atmosphere:	Argon

Table 1: *Milling parameters of the experiments for all processing durations*

2.4 Results (SEM, XRD)

The results for the experiments up to a milling interval of 10 h can be seen as follows by SEM and XRD:
After a duration of 5 hours the particle shape has completely changed compared to those of the starting powders. Since the other investigated powders only vary a little concerning their powder compositions, the evolution of the particle size distribution only of the Ti-50Ni powder processing will be shown in the following:

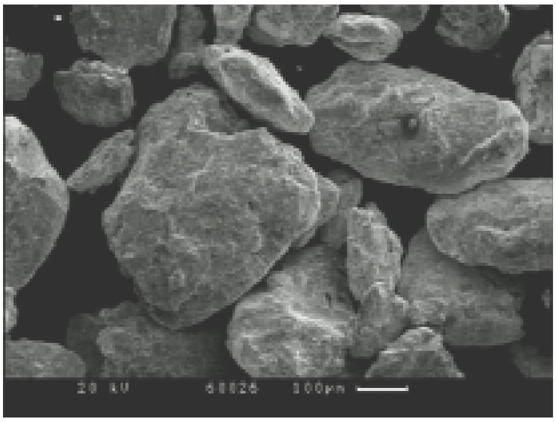

Fig. 4.a: *Processed powder after 5 hours*

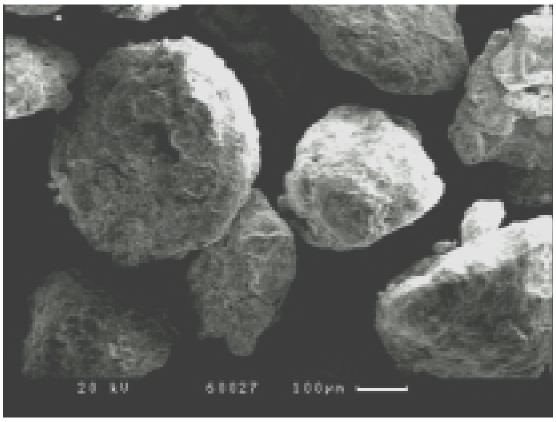

Fig. 4.b: *Processed powder after 6 h*

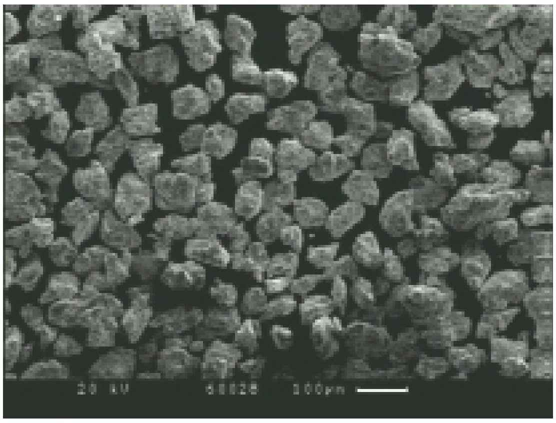

Fig. 4.c: *Processed powder after 7 h*

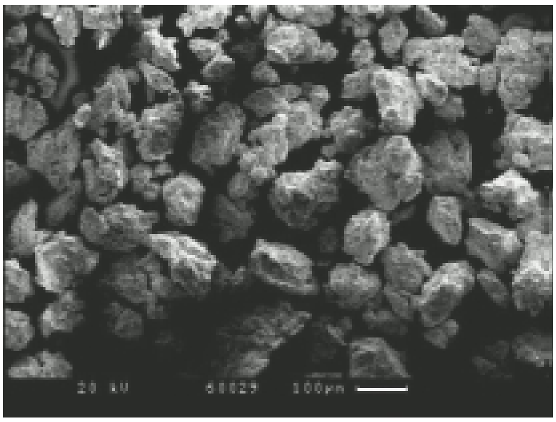

Fig. 4.d: *Processed powder after 8 h*

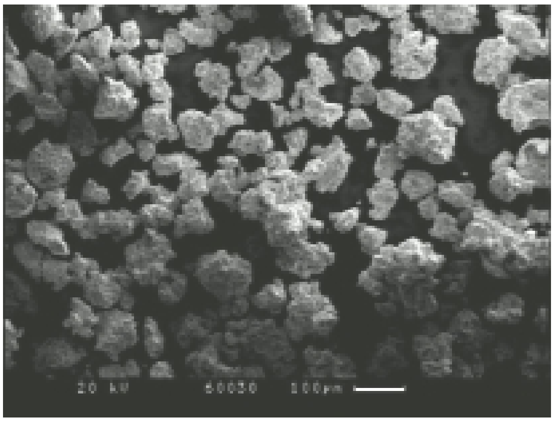

Fig. 4.e: *Processed powder after 9 h*

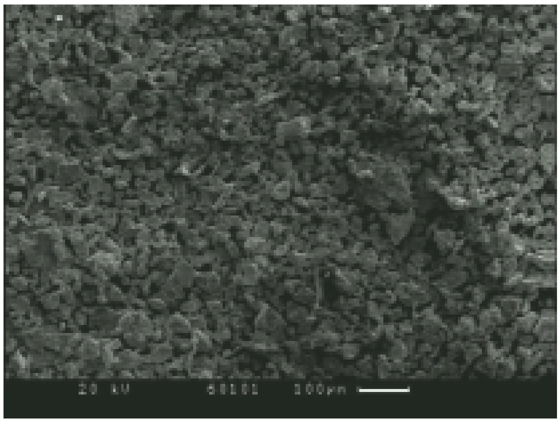

Fig. 4.f: *Processed powder after 10 h*

It can be seen by the *Fig. 4.a to 4.f* that the particle shape completely changes during the milling process. After 5 hours of processing the powder particles exhibit a broad size distribution with values of 100 to 400 microns and flat particle shape. 1 hour later the particle size has increased to values from 200 to 400 microns. The particle surface is fissured and irregular. A remarkable change can be noticed after 7 hours: the particle size is reduced to about 60 microns due to a further phase homogenization. After 8 hours the particle size is increasing to values of 100 microns again. 1 hour further processing leads to fractured particles with an average size value of 80 microns. The SEM micrograph of the final powder extraction after 10 hours shows particle sizes of 20 microns and lower. By this result the beginning of the final alloying process and a homogenization of the phases can be assumed. However, the formation of an amorphous phase could not be observed after 10 hours. This is also represented by the XRD patterns (*Fig. 5*). A similar evolution of the particle size could be recognized in the case of the other compositions Ti-49.5Ni and Ti-48.5Ni. In particular it can be noticed that the particle sizes are first enlarged, then reduced, further enlarged again during processing, until they are finally reduced to lower values.

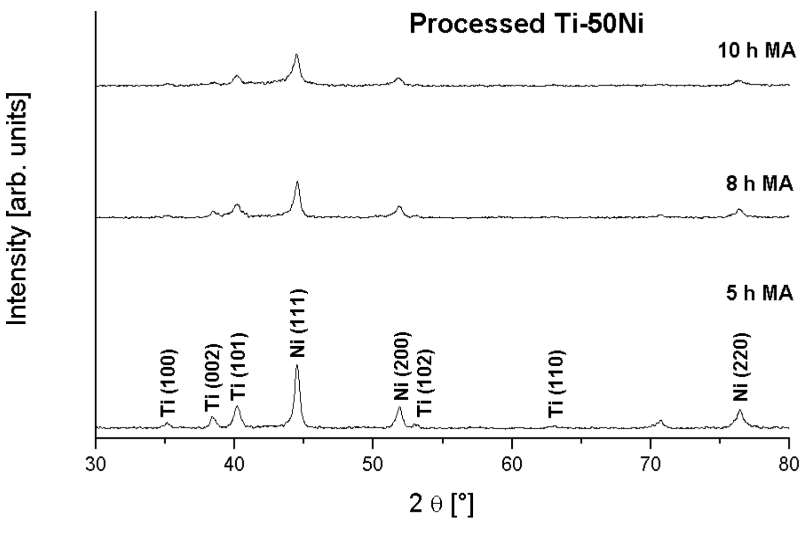

Fig. 5: *X-ray diffraction patterns of the processed Ti-50Ni powder after 5, 8 and 10 hours*

3. Discharging / Powder Yield

3.1 Ti-Ni-Compositions, Ductility, CMB

By experience Ti and Ni powders show a critical milling behavior (CMB) when processed on the powder metallurgical route. Sticking to the milling balls, the grinding chamber and the rotor of the Simoloyer due to their ductile behavior, the first consequence is that a large amount of powder is stored in layers, where no further processing can take place. The second consequence is a sensitive change of the component concentration of the remaining powder rest which is processed. In the end of the mechanical alloying process only a low powder yield can be obtained, as a large amount of powder remains in the milling device. If the use of milling agents would pollute the material, the only way to achieve an acceptable powder yield is to apply a suitable milling process following a special program.
In a previous work (Ti-24Al-11Nb, ISMANAM-96, Rome) it has been shown that Cycle Operation Procedure has an enormous influence on the achievable powder yield as well as on the processing itself. Therefore the Cycle Operation is used for the Ti-Ni compositions as well.

3.2 Solution: Cycle Operation

The idea is to process those powders by applying cyclic varied rotational speeds in order to break the balance of deformation, fracture and welding in the process.
In *Fig. 6.a* and *6.b* the used milling and discharging cycles can be seen. The shown Operation Cycles were applied on the milling experiments of 1, 2, 5, 6, 7, 8, 9 and 10 hours.

3.3 Used Cycles

An operation cycle in this case is characterized by a time interval of 4 min at 1500 min^{-1} followed by 1 min at 900 min^{-1}. Having passed the last milling interval at 10 h a final Discharging Cycle was realized followed by *Fig. 6.b*. A discharging cycle was composed by an interval of 4 min at a rotational speed of 900 min^{-1} and an interval of 1 min at 1500 min^{-1}.

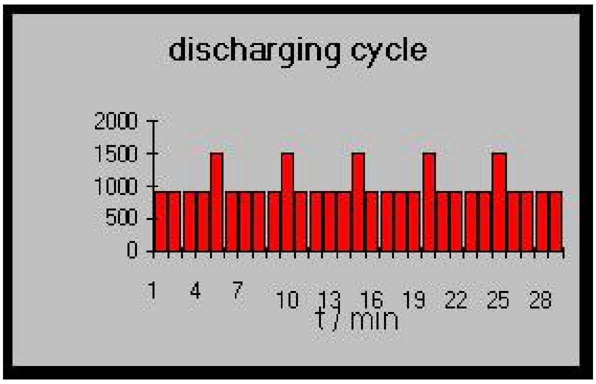

Fig. 6.a: Operation Cycle used for processing

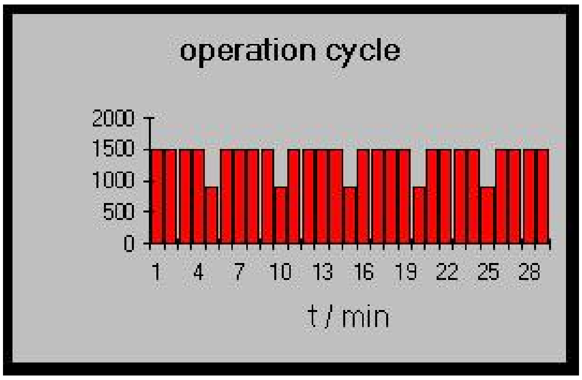

Fig. 6.b: Discharging Cycle used for discharging

The following results were achieved by this way:

3.4 Achieved Powder Yields / Results

The achieved powder yield of this problematic alloying system which is represented by the following diagram (*Fig. 8*) is of high interest:
Although showing a critical milling behavior (CMB) and being processed for a large time interval, a large amount of processed Ti-Ni powder has been received following the special discharging procedure. As a successful result for a yield of 70 % of powder was reached after 50 minutes approx. of discharging for the Ti-50Ni composition. For the Ti-49.5N respectively the Ti-48.5Ni composition the yield has been lower after the same discharging time. This is due to the fact that the wall of the milling chamber has been coated during the first milling procedure of the Ti-50Ni composition. The enlarged surface and the roughness of the coated wall leads to an increasing adhesion of the processed powder during the following milling processes with the consequence of a reduced yield after processing. That shows the importance of smooth and clean container walls. This fact proves that the milling parameters can sensitively influence the milling behavior and consequently the milling results.

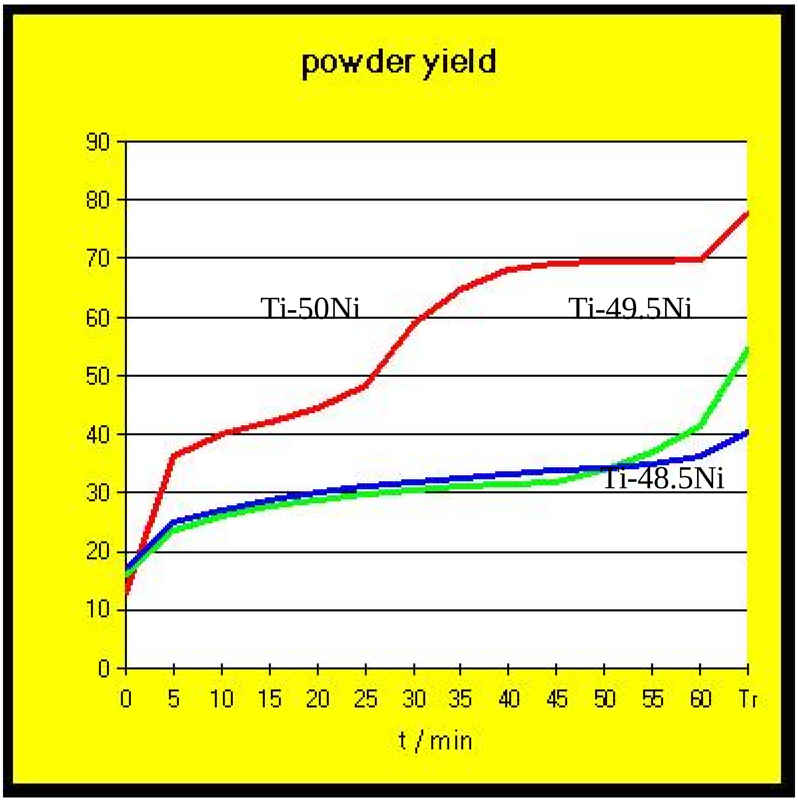

Fig. 8: Powder yield after 10 h of processing

4. Conclusions

Mechanical Alloying is a forward looking technology with a wide range of applications using various systems. Often these materials show a Critical Milling Behavior (CMB) due to their ductility. As an example Ti-Ni powders have been processed for several time intervals.
In previous work based on Ti-24Al-11Nb material [6], it has been shown that Cycle Operation has an enormous influence on the achievable powder yield as well as on the processing itself. In case of the here discussed Ti-Ni compositions a similar behavior is noticed. The achieved powder yield in case of the Ti-50Ni has been about 70 % after a discharging time of 50 min approx., which is not as good as the result in the mentioned previous work (80 % / 60 min) but still a remarkable result. The lower yield of the Ti-49.5Ni and the Ti-48.5Ni compositions is probably caused by the increasing coating of the vessel by the trials themselves and the following enlargement and roughness of the surface. This shows that here it has not been possible to avoid a coating of the vessel absolutely. This has to be improved by optimization of the Cycle Operation procedure.

5. References

[1] J.S. Benjamin, Metall. Trans., Vol. **1**, 2943 (1970)

[2] J.S. Benjamin, T.E. Volin, Metall. Trans. Vol. **5**, 1929 (1974)

[3] P.G. McCormic, H. Huang, M.P. Dallimore, J. Ding, J. Pan, *The Dynamics of Mechanical Alloying, Structural Applications of MA*, ASM, eds. J.J. Barbadillo, F.H. Froes, R.B. Schwarz, 1993

[4] D. Ernst, H. Weiss, H. Zoz, *Structure and Properties of Nanophase Materials*, TMS, eds. B.T. Fultz, C.C. Koch, P.J. Maziasz, R.D. Shull, 1995

[5] C. Suryanarayana, Guo-Hao Chen, F.H. Froes, *Milling Maps for Phase Identification during Mechanical Alloying*, Scripta Metallurgica et Materialia, Vol. **26**, 1727 (1992)

[6] H. Zoz, D. Ernst, H. Weiss, M. Magini, C. Powell, C. Suryanarayana, F.H. Froes, *Mechanical Alloying of Ti-24Al-11Nb (at%) using the Simoloyer (Zoz - horizontal rotary ball mill), Part I,* ISMANAM 96 / proceedings pp, Rome, Italy