MECHANICAL ALLOYING OF TI-24AL-11NB (AT%) USING THE SIMOLOYER*

(* *Zoz - horizontal rotary ball mill*)

H. Zoz[1], D. Ernst[2], H. Weiss[2], M. Magini[3], C. Powell[4], C. Suryanarayana[4], F.H. Froes[4]

[1]Zoz GmbH, D-57223 Kreuztal, Germany. [2]University of Siegen, D-57068 Siegen, Germany.
[3]ENEA, INN/NUMA, C.R. Casaccia - Rome, Italy.
[4]Inst. f. Materials and Advanced Processes, University of Idaho, Moscow, Idaho 83844-3026.

Abstract

The production of large quantities of contamination free mechanically alloyed powders from titanium 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-24Al-11Nb (at%) powder 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 steel balls. 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 Behaviour (CMB) of the system under investigation that must be kept under control to achieve the wanted goal. It will be shown that by adopting a suitable milling and discharging procedure low contamination and good yield have been substantially achieved with respect to preliminary not unambiguous trials carried out at Idaho university.

1. Introduction

During the last years the mechanical alloying technique 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 receiveable by conventional processing techniques due to e.g. the immiscibility of their components.
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.

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 Behaviour (CMB). 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 the elemental Ti-24Al-11Nb (at%) powder which was processed in a Simoloyer for experimental investigations. Some preliminary not unambiguous trials with low powder yield carried out at Idaho university were the motivation for those further experiments with a suitable milling and discharging procedure.

2. Mechanical Alloying of Ti-24Al-11Nb (at%)

2.1 Starting Powders

The starting powder Ti-24Al-11Nb (at%) was a powder blend of elemental Ti-powder and prealloyed Al-Nb powder. The starting powders and the evolution of the milling process was 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_α radiation. *Fig. 1.a* and *Fig. 1.b* show the particle shape of elemental Ti and Al-11Nb starting powder.

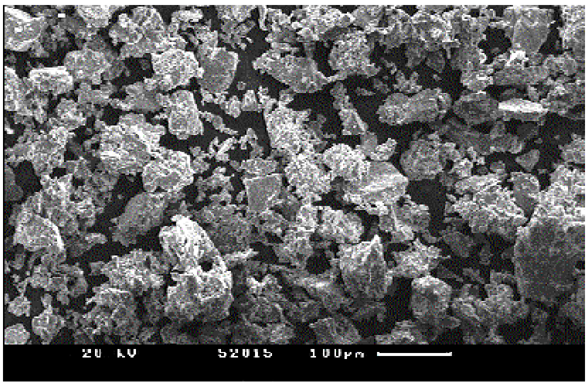


Fig. 1.a: Ti starting powder

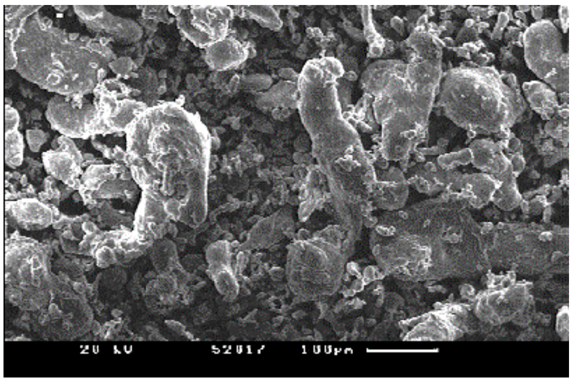


Fig. 1.b: Al-11Nb starting powder

It can be seen that both starting powders are characterized by broad particle size distributions. In the case of Ti the sizes vary from low sizes of a few microns up to sizes of 100 microns. The particle shape is fissured and irregular. The Al-11Nb starting powder exhibits particle sizes from also a few microns up to 300 microns of the largest particles. Their geometries are of spherical and cylindrical shape. The X-ray diffraction pattern in *Fig. 2* proves the presence of crystalline phases.

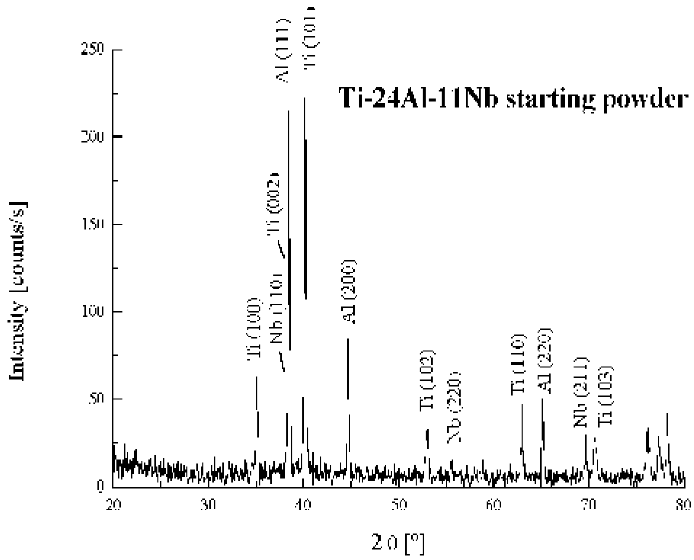


Fig. 2: X-ray diffraction pattern of the starting powder blend

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*).

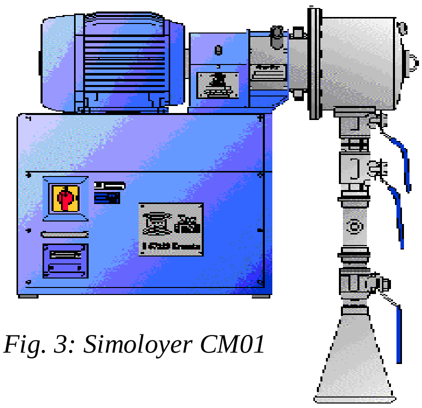


Fig. 3: Simoloyer CM01

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.

2.3 Milling Parameters

First the starting powders were premixed in the composition of Ti-24Al-11Nb (at%). To avoid reactions with oxygen and nitrogen the powders were handled in a glove box under inert gas atmosphere (argon). An amount of 130 g of premixed powder was then filled into the charging can. 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 20 min, 1, 3, 5, 10 and 15 hours were carried out and the resulting powders were investigated by SEM and XRD. Since the tests from the time interval from 20 min up to 5 hours were followed by a constant rotational speed of 1300 revolutions per minute, the two last tests (10 h and 15 hours) were prepared by a special milling cycle.

After 10 hours of processing time 5 g of the resulting powder were extracted for investigation. The final powder discharging procedure was carried out by a special discharging cycle to receive a high yield (see section 3).

Simoloyer:	CM01-0.5 l with water-cooled container
Milling balls:	Material: steel (100Cr6)
	Diameter: 5.1 mm
	Total weight: 1300 g
Weight of powder charge:	130 g
Powder/ball-weight ratio:	1:10
Rotational speed:	1300 min^{-1}
Milling atmosphere:	Argon

Table 1: Milling parameters of the experiments for the time intervals of 20 min, 1, 3 and 5 h

2.4 Results

The results for the experiments up to a milling interval of 5 h can be seen as follows by SEM and XRD:
After a duration of 20 min the particle shape has completely changed compared to those of the starting powders.

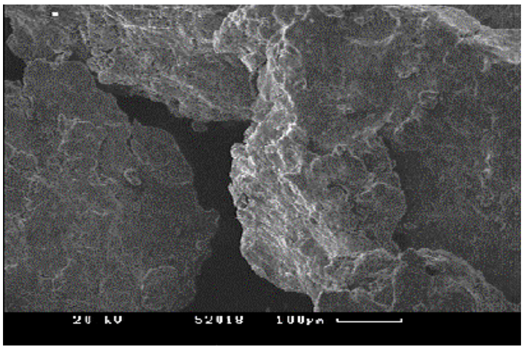


Fig. 4.a: Processed powder after 20 min

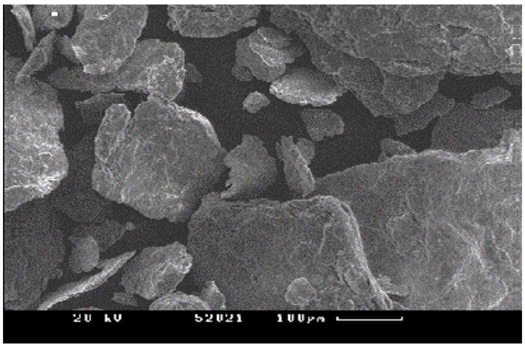


Fig. 4.b: Processed powder after 1 h

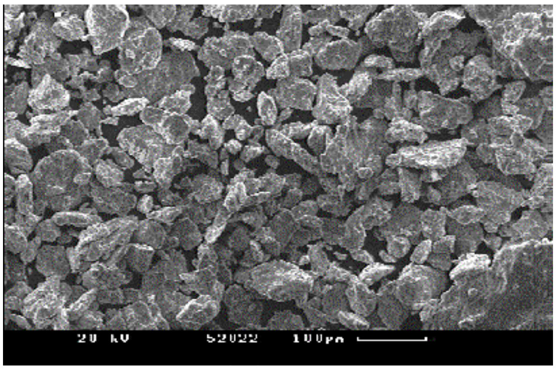


Fig. 4.c: Processed powder after 3 h

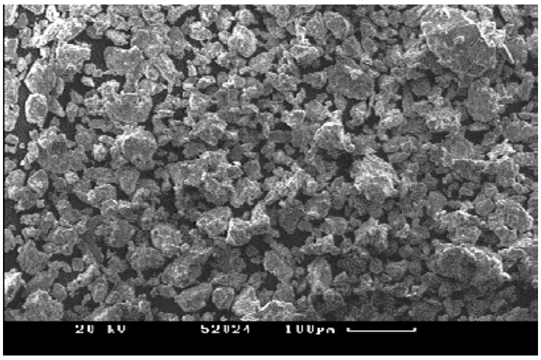


Fig. 4.d: Processed powder after 5 h

5 hours later the particle size has been reduced to an average particle size of 30 microns. A homogenization of the phases can be observed by the XRD pattern (*Fig. 5*). Unfortunately the powder yield has been very low in all cases so that a special milling and a discharging cycle has to be concerned.

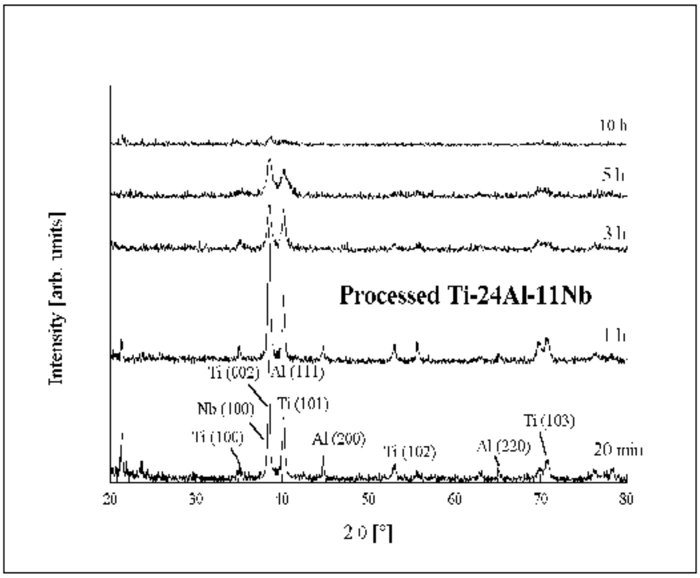


Fig. 5: X-ray diffraction patterns of the processed powder

A phase transformation into an fcc crystal structure can be assumed by the above X-ray diffraction patterns between 10 and 15 hours as found by *Suryanarayana et al.* for Ti-33Al. After 15 hours of mechanical alloying any reflexes are absent.

3. Powder Yield of the Process

3.1 Ti-24Al-11Nb - A ductile Material with CMB, Difficulties

By experience Ti and Al powders show a critical milling behaviour (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 behaviour, 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.
During these experiments the final powder yield has been substantially improved by a so called *cycle operation*.

3.2 Improvement of the Powder Yield by 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 milling cycles were applied on the milling experiments of 10 and 15 h.

An operation cycle in this case is characterized by a time interval of 4 min at 1300 min^{-1} followed by 1 min at 900 min^{-1}. Having passed the last milling interval at 15 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 1300 min^{-1}.

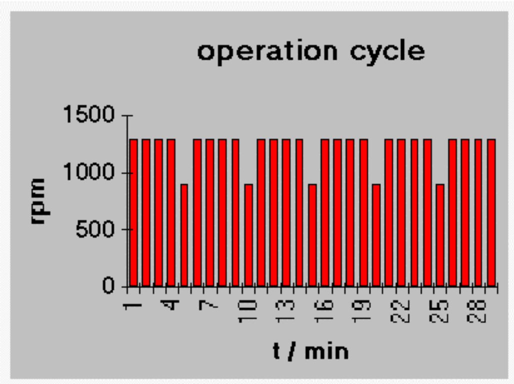


Fig. 6.a: Operation cycle used for processing

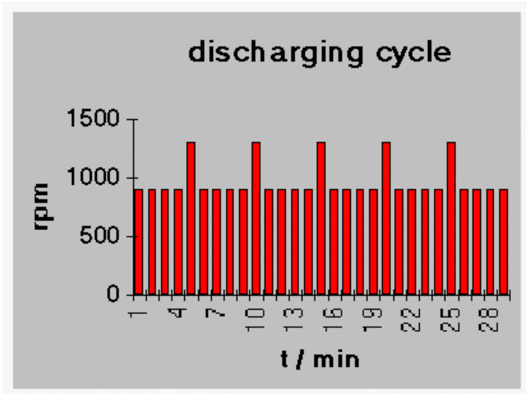


Fig. 6.b: Discharging cycle used for discharging

The following results were achieved by this way:

3.3 Results

The received particle sizes are shown in the following SEM-micrographs:

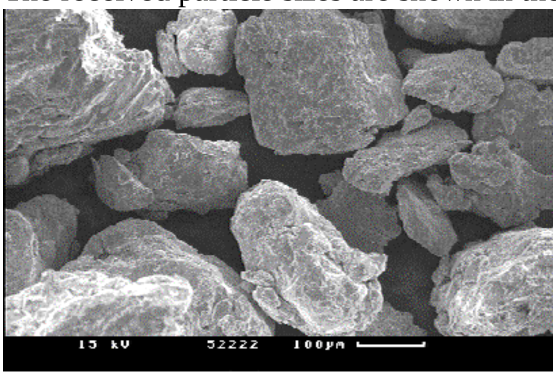


Fig. 7.a: Processed powder after 10 h using cycle operation

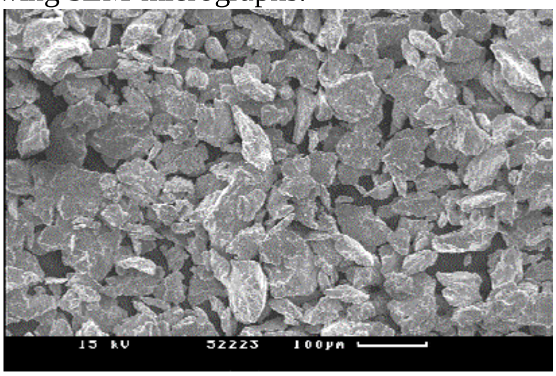


Fig. 7.b: Processed powder after 15 h using cycle operation

After 10 hours of mechanical alloying the particle sizes have average values of about 150 microns. 5 hours later and after a total milling time of 15 h, the particle sizes were reduced to values of about 30 microns.

The achieved powder yield of this problematic alloying system which is represented by the following diagram (*Fig. 8*) is of high interest:

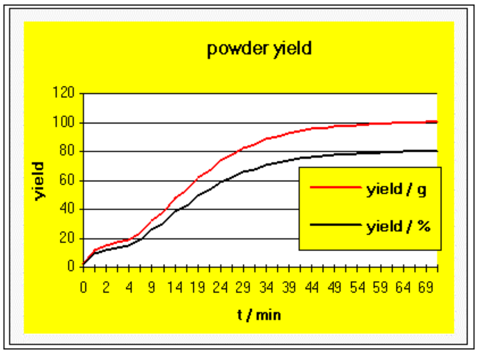
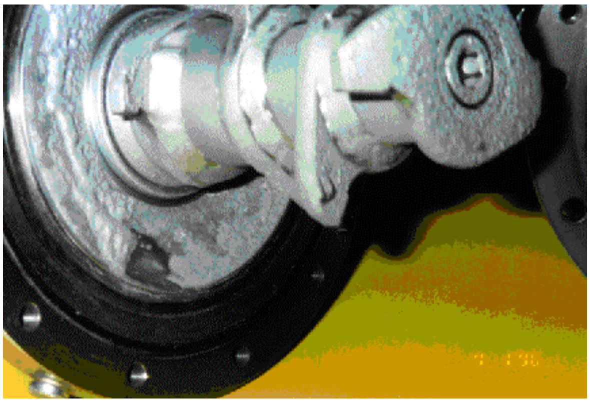


Fig. 8: Powder yield after 15 h of processing

Although showing a critical milling behaviour (CMB) and being processed for a large time interval, a large amount of processed Ti-24Al-11Nb powder has been received following the special discharging procedure. As a successful result a yield of 80% (100 g) of powder was reached after 64 minutes of discharging. This fact proves that the milling parameters can sensitively influence the milling behaviour and consequently the milling results.

The view inside of the grinding chamber confirms these results:
Figure 9.a + b show the rotor, flange and the vessel after preliminary trials with Ti-24Al-11Nb using an ordinary operation procedure with constant parameters. Most of the powder sticks on the chamber walls, the rotor and the grinding media which is the easy explanation for the very low powder yield after the process. The only way to get the powder out again is to machine it out as shown on *Figure 10.a + b*.



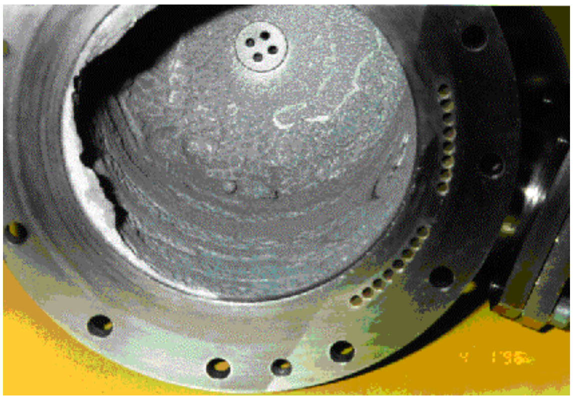
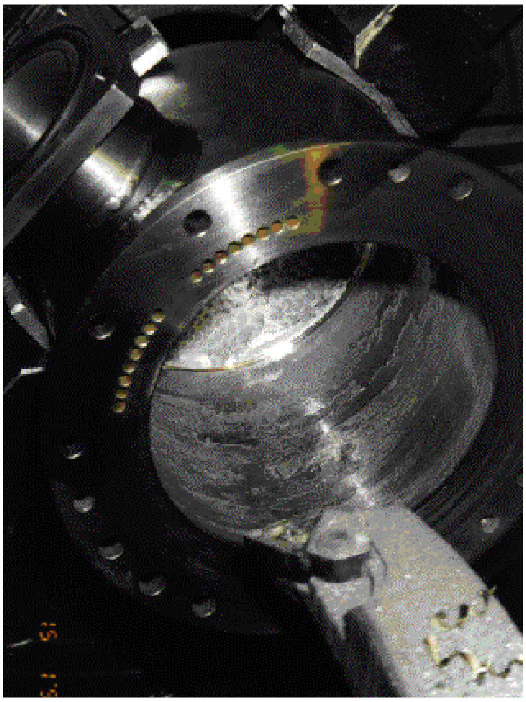


Fig. 9.a + b: Grinding chamber after operation with constant parameters



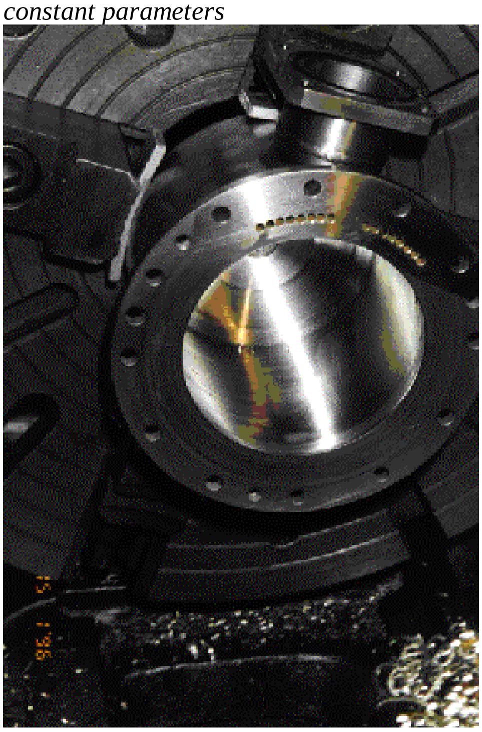


Fig. 10.a + b: Mechanical removal after constant operation

Figure 11.a + b show the rotor, flange and the vessel after 16 h processing Fe_3Al-base materials with yttria additions for dispersion strengthening using a similar cycle operation as applied here for the Ti-24Al-11Nb material. As there are no photos of the here used grinding unit after the cycle operation available yet, this example is used. The pictures have recently been taken at Oak Ridge National Laboratory in Tennessee. Fe_3Al shows also a high ductility with CMB and causes the same difficulties as described before when using an ordinary operation procedure with constant parameters. The pictures *Figure 11.a + b* prove that only a very small amount of powder is becoming compacted against the chamber wall when using cycle operation.

Fig. 11.a+b: Grinding chamber after cycle operation (Fe_3 Al, Oak Ridge National Laboratory, Oak Ridge, TN)

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 Behaviour (CMB) due to their ductility. As an example Ti-24Al-11Nb powder has been processed for several time intervals.
It has been shown how to improve the process by adopting variable operation and discharging parameters (Cycle Operation).
The possibility of scaling up is a need for every process regarding any industrial application. One consequence is the demand for a high powder yield, short processing times and low contamination rates.
The contamination has not yet been investigated.
The cycle operation procedure for discharging as well as for operation with its enormous influence on the achievable powder yield has been explained.
It is not expected, that the change of milling behaviour is a consequence of a oxygen pick up with a following increasing embrittlement of the powder, as the Simoloyer (Zoz - horizontal

rotary ball mill) avoids any oxygen pick up from outside and the starting powder was announced to have a very low oxygen content.

In case of Ti-24Al-11Nb, the achieved yield has been about 80 % after a discharging time of 60 min approx., which is a remarkable result. Further optimization seems possible.

5. References

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

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

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

[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] 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