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MECHANICAL ALLOYING USING CYCLE OPERATION - A NEW WAY TO SYNTHESIZE CMB-MATERIALS -

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Abstract

The production of large quantities of contamination free mechanically alloyed powders 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 large volume units (up to 400 l) based on the same conceptual design.
A lot of the mechanically alloyed advanced materials show a critical milling behavior due to their ductility. To be able to process these kind of powders nevertheless, milling agents or / and deep temperature milling have been applied in the past. Today these difficulties and limits are solved by the cycle operation procedure using the so called Operation Cycle and Discharging Cycle for the processing.
The present paper will focus on the results of several experiments on titanium, nickel, silver and aluminum based Materials. This is investigated by chemical analysis, by scanning electron microscopy and X-ray diffraction.
A proved powder yield over 80 % and a homogeneous and reproducible product allows to consider an industrial production. From the economical point of view, this should finally be a continuous process.

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 receivable by conventional processing techniques due to e.g. the immiscibility of their components.
Often ductile powder components are combined with brittle components. In most cases a combination of those powders is critical due to the inherent adhesion tendency of the powder sticking to the grinding unit and the steel balls. Unfortunately a lot of alloying systems identify such a Critical Milling Behavior (CMB).
This paper is a summary of two previous projects on MA of materials of a high ductility and focuses on therein approached possibilities given by Cycle Operation procedure.

2. CMB-Materials - Challenge and Difficulties

Materials with CMB, which means ductile materials like titanium, nickel, silver and aluminum based powders are of high interest for industrial applications, e.g. in aerospace, electrical components, metallic paints, etc. and are increasingly produced on the powder metallurgical route. Being processed in conventional ball milling devices those powders exhibit difficult properties: In most cases the powder yield after processing is very low because of the high adhesion tendency of the powders. This is due to the fact that the powders stick to the milling balls, the grinding chamber and other parts of the milling device. 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. Furthermore, if the use of milling agents would pollute the material, the only way to achieve an acceptable powder yield is to use a suitable milling device and to apply a special milling process which also allows a scaling-up to an industrial application with an efficient powder yield, short processing times and low contamination rates.

3. The Processing

3.1 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.

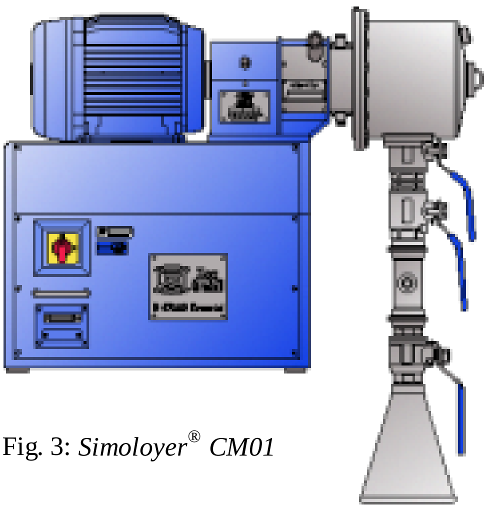

Fig. 3: *Simoloyer® CM01*

3.2 Milling Parameters

If Mechanical Alloying is regarded as a repeated deformation, fracture and welding by highly energetic ball collisions, a high and homogeneous kinetic energy impact is necessary. To achieve this aim, a high rotational speed of the rotor of the rotary ball mill (Simoloyer) is needed. The availability of free space for free movement of the milling balls after any impact is performed by a total filling ratio of 40 % and below. Together with the nonexistence of deadzones, the aim is achieved and the wanted high degree of deformation and welding will cause new difficulties as the powder will coat the milling tools and the vessel in dead layers.

These layers have a similar bad influence as dead zones. They can be avoided by frequently interruption of the impact. The idea is to break the balance between deformation, fracture and welding in the process. The procedure is called Cycle Operation.
Since the here discussed powders mostly have to be clean powders, the processing and the powder handling, this means milling and charging and discharging have to be performed under defined conditions like vacuum or inert gas atmosphere to avoid reactions of the processed powder with oxygen and nitrogen. This is realized by the use of an air-lock with an advanced draingrating system.
As well the temperature of the grinding chamber unit has to be controlled by a cooling system as the high energy impact causes an increasing powder temperature that has to be compensated by the device. Sometimes even an external increase of the temperature is necessary, e.g. to favor a chemical reaction.

4. The Materials Ti-24Al-11Nb and Ti-50Ni

4.1 Starting powders

Several milling experiments have been carried out with titanium based alloys, especially Ti-24Al-11Nb and Ti-50Ni powders which are very difficult being processed by ball milling due to CMB. 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_α radiation.
The starting powder Ti-24Al-11Nb (at%) was a powder blend of elemental Ti-powder and prealloyed Al-Nb powder. *Fig. 2.a* and *Fig. 2.b* show the particle shape of elemental Ti and Al-11Nb starting powder.

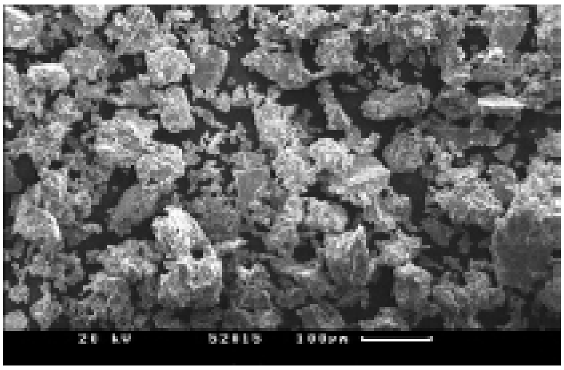

Fig. 2.a: *Ti starting powder*

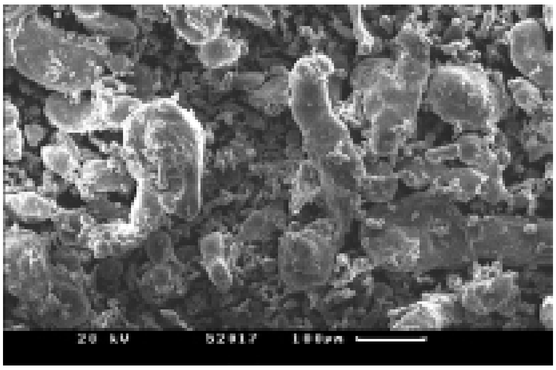

Fig. 2.b: *Al-11Nb starting powder*

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 geometry are of spherical and cylindrical shape. The X-ray diffraction pattern in *Fig. 3* proves the presence of crystalline phases.

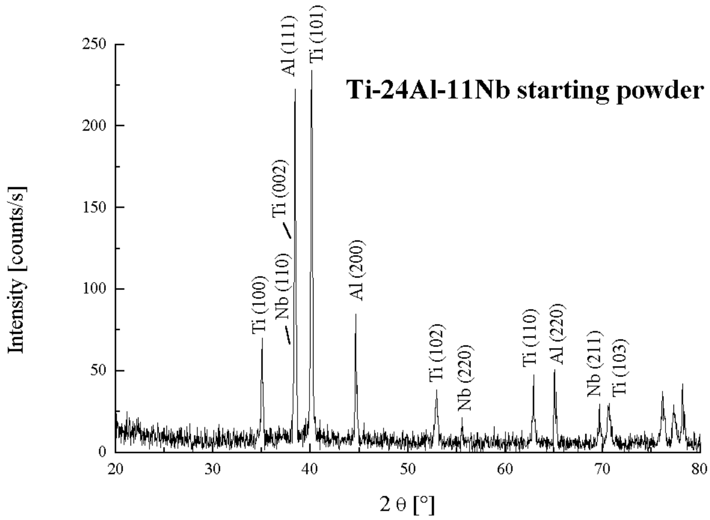

Fig. 3: X-ray diffraction pattern of the Ti-24Al-11Nb starting powder blend

The Ti-50Ni starting powder was a powder blend of elemental Ti-powder and elemental Ni-powder. The SEM-micrograph in *Fig. 4.a* and *Fig. 4.b* show the particle shape of the elemental Ti and Ni starting powder.

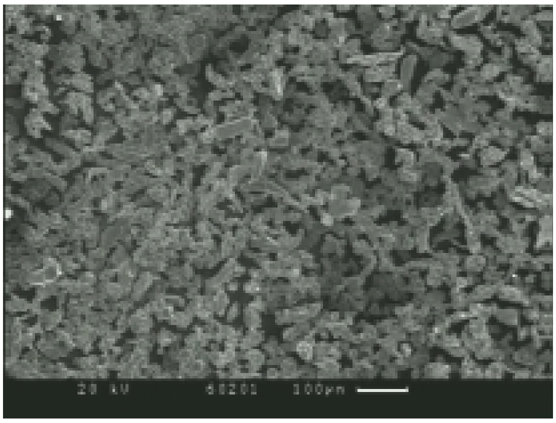

Fig. 4.a: Ti starting powder

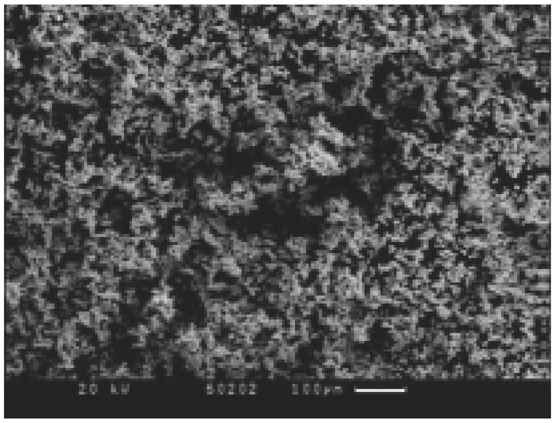

Fig. 4.b: Ni starting powder

The sizes of the Ti particles vary from 40 microns up to sizes of 100 microns and in case of the Ni starting powder particle sizes with regular shape about 10 microns can be observed. It can also be seen by the X-ray diffraction pattern in *Fig. 5* that crystalline phases are present.

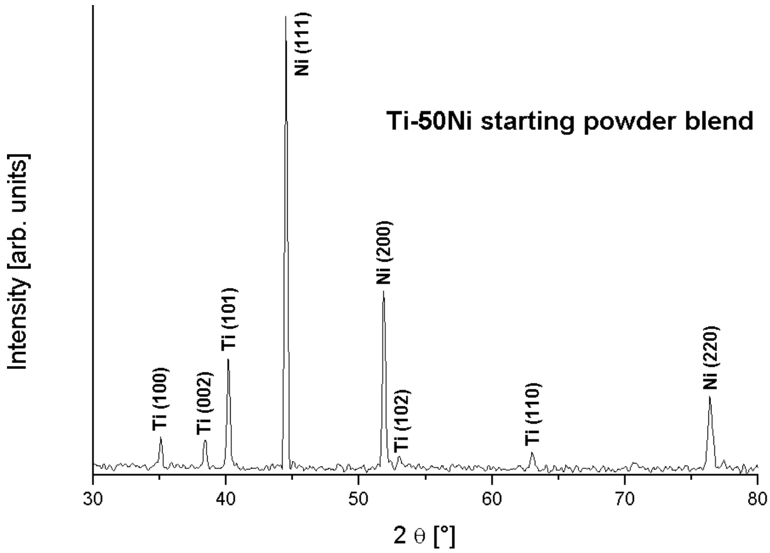

Fig. 5: *X-ray diffraction pattern of the Ti-50Ni starting powder blend*

4.2 Milling Parameters

To avoid reactions with oxygen all powders were handled and processed under inert gas atmosphere (argon). The powder to ball weight ratio for all powders was chosen as 1:10 and the used conventional steel balls (100Cr6) had an average diameter of 5.1 mm.
For the Ti-24Al-11Nb alloying system milling intervals from 20 min up to 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 Cycle Operation (see *Table 1)*.
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 4.3).

Simoloyer:	CM01-1/2 l	
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 / 900 min^{-1} (cycle)	
Milling atmosphere:	Argon	

Table 1: *Milling parameters of the Ti-24Al-11Nb experiments for the time intervals of 10 and 15 h*

The Ti and Ni starting powders were premixed in the composition of Ti-50Ni (at%) and an amount of 100 g of premixed powder was processed for each test (see *Table 2*). Several milling intervals from 1 to 10 hours were carried out and the resulting powders were investigated by SEM and XRD afterwards. Since the Ti-50Ni powder also show a CMB due to its 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 4.3 / 4.4).

Simoloyer:	CM01-1/2 l	
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 2: *Milling parameters of the Ti-50Ni experiments for all processing durations*

4.3 Operation and Discharging Cycles

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 has been used for the powder processing.
Cycle Operation Procedure means to apply 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 operation and discharging cycles of the Ti-50Ni experiments can be seen. The shown operation cycle was applied on the milling experiments after the 10 h processing time in case of the Ti-50Ni powder.
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}.

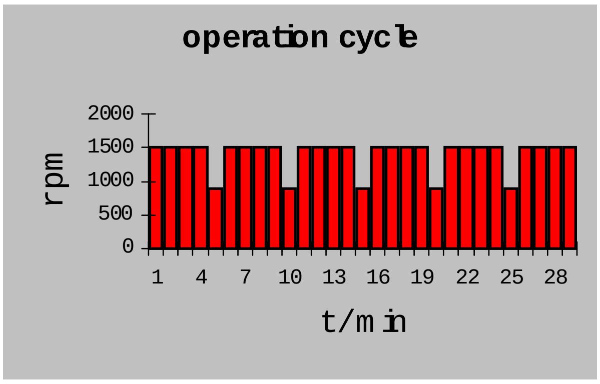

Fig. 6.a: *Operation cycle Ti-50Ni*

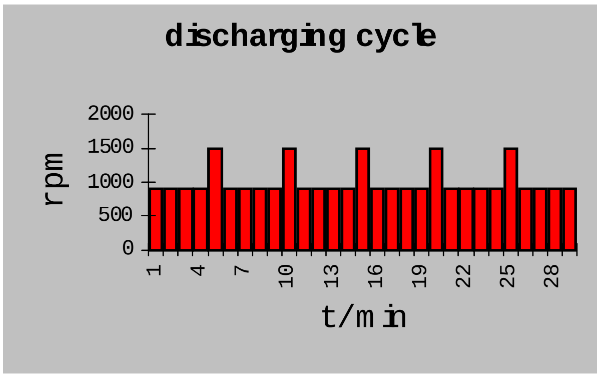

Fig. 6.b: *Discharging cycle Ti-50Ni*

The following results were achieved by this way:

4.4 Processed Powders

The results for the experiments of the processed Ti-24Al-11Nb and Ti-50Ni can be seen as follows by SEM and XRD:
After a short duration of milling the particle shape of both investigated powders has completely changed compared to those of the starting powders.

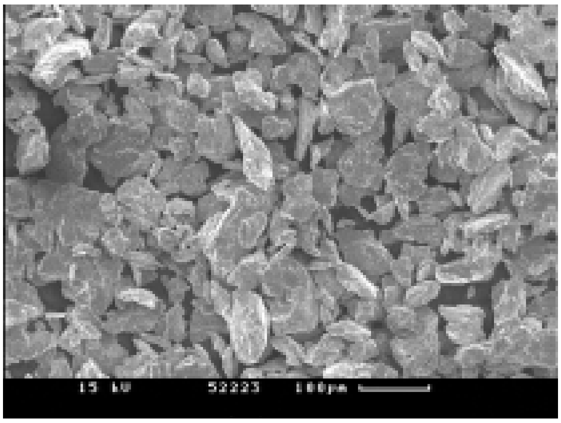

Fig. 7.a: *Ti-24Al-11Nb: powder after 15 h*

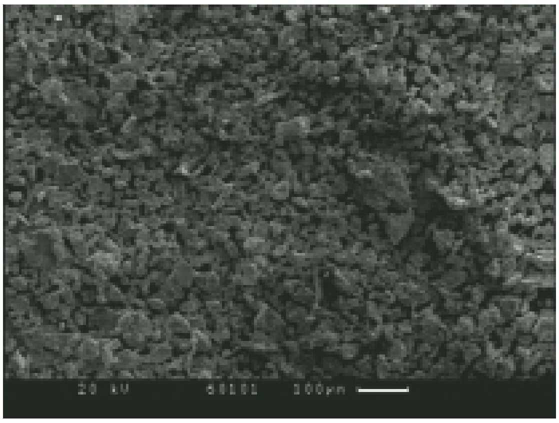

Fig. 7.b: *Ti-50Ni: powder after 10 h*

In the case of the Ti-24Al-11Nb the particle size has been reduced to an average value of 30 microns after a total milling time of 15 h. The SEM micrograph of the final Ti-50Ni powder extraction after 10 hours shows particle sizes of 20 microns and lower. Both results indicate the beginning of the final alloying process and a homogenization of the phases. This is also represented by the XRD patterns (*Fig. 8.a / 8.b*).

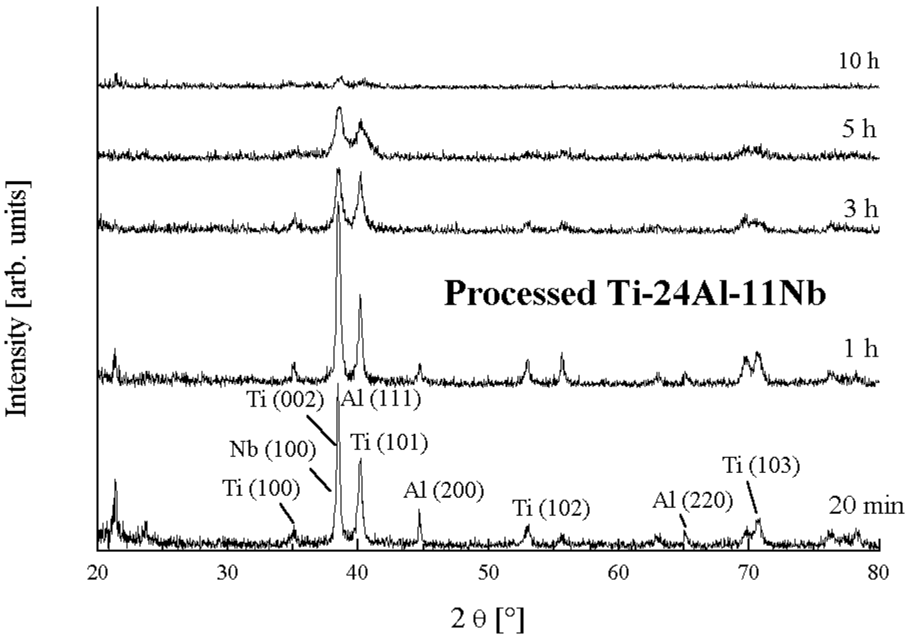

Fig. 8.a: *X-ray diffraction patterns of the processed Ti-24Al-11Nb powder*

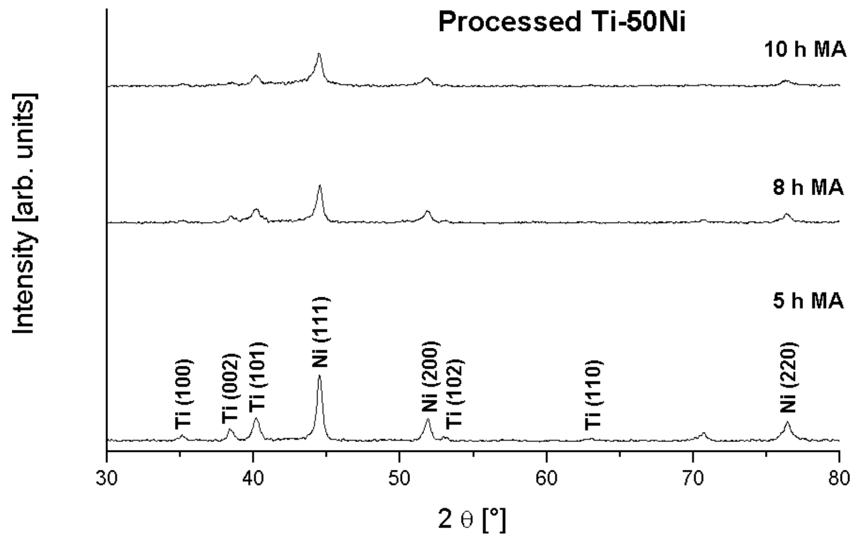

Fig. 8.b: *X-ray diffraction patterns of the processed Ti-50Ni powder*

4.5 Powder Yield and Chemical Analysis

The achieved powder yields of these problematic alloying systems which are represented by the following diagram (*Fig. 9.a and 9.b)* is of high interest:
Although showing a critical milling behavior (CMB) and being processed for a large time interval, large amounts of processed Ti-24Al-11Nb and Ti-50Ni powder have been received following the special discharging procedure. As a successful result of a yield of 80 % powder was reached for the Ti-24Al-11Nb after 64 minutes of discharging and a yield of 70 % for the Ti-50Ni after 50 minutes approx. has been achieved. This fact proves that the milling parameters can sensitively influence the milling behavior and consequently the milling results.

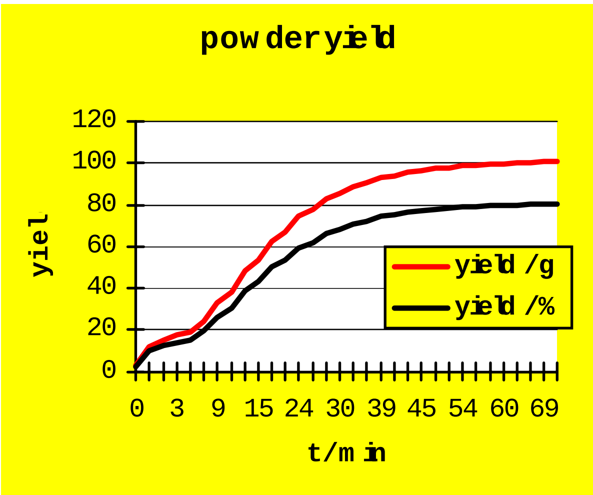

Fig. 9.a: *Powder yield for the Ti-24Al-11Nb system after 15 h of processing*

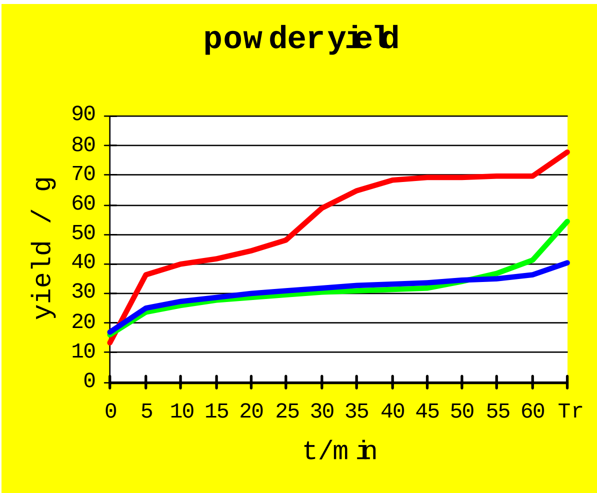

Fig. 9.b: Powder yield for the Ti-50Ni system

The chemical analysis of the Ti-24Al-11Nb powder shows that the oxygen respectively nitrogen pickup during processing with average values of 0.279 wt.% respectively 0.058 wt.% was very low since the initial powder had values of about 0.067 wt.% oxygen and 0.0050 wt.% nitrogen. This is a remarkable result especially because Ti powders with small particle sizes usually show high reaction rates with oxygen due to their affinity. For the Ti-50Ni composition, these results are not yet available. The powder yield in case of Ti-Ni composition is similar:

5. Various Applications - Example: Reactive Milling of Ag_3Sn + Ag_2O

Further investigations have been done on the system Ag_3Sn / Ag_2O which is very interesting for industrial application in electrical components (contact material). During the milling process in the Simoloyer, a chemical reaction is started that leads to a highly dispersed tin oxide phase in a silver matrix (see *Fig. 10*). The reaction depends on the temperature (heating recommendable) and the kinetic of the milling process. This powder extremely exhibits CMB. Without Cycle Operation Procedure, no useable results can be obtained. After optimization of the milling parameters and applying Cycle Operation, however, it is possible to achieve a very high powder yield of nearly 95 % of the processed powder. Only very short milling times are necessary and consequently the contamination is not problematic.

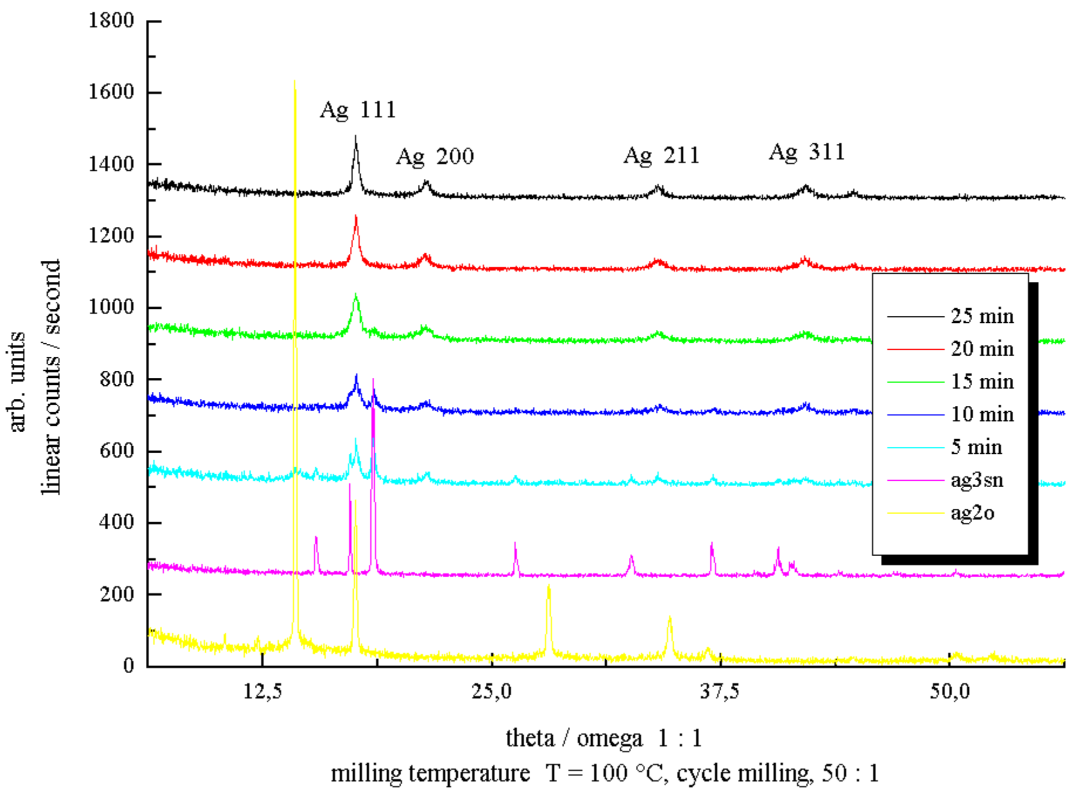

Fig. 10: *X-ray diffraction pattern of the processed Ag_3Sn/Ag_2O powder*

5.1 Unexpected Behavior during High Temperature Milling

Various experiments have been carried out under different temperature conditions to optimize the reaction and the powder yield. Previous tests have shown that a high milling temperature favors the reaction kinetic and shortens the milling process.
During these experiments an unexpected behavior of the powder occurred: during a trial almost all of the powder stuck to the milling tools and the vessel at a dedicated time. Somehow later in the process this adhesion behavior disappeared until it appeared again later on. This effect occurred repeatedly.

5.2 Experiments with Video-equipment during Processing (Approach)

As there is no explanation for this effect so far, investigation of the process by a video-equipped grinding unit has been started. A small size video camera as well as a stroboscope have been connected to the grinding chamber in a dedicated angel, in order to film this part of the vessel where mostly the adhesion occurred. The equipment is prevented by glass-sheets and is fitted gas-tight to the system.

6. Conclusions I

Mechanical Alloying/ High Energy Milling of ductile materials is very interesting due to its various industrial application possibilities, e.g. in aerospace, electrical components, metallic paints, etc. To find any real application, a reproducible scaling-up of the laboratory use is necessary.
As these materials show a Critical Milling Behavior (CMB) due to their ductility, a standard ball milling procedure does not lead to suitable results.
Using the examples of Ti-24Al-11Nb and Ti-50Ni compositions, the enormous influence of the Cycle Operation Procedure on the achievable powder yield as well as on the processing itself has been shown.
It has been explained how Mechanical Alloying / High Energy Ball Milling can be used efficiently and lead to clean powders using a Simoloyer.
In case of the Ti-24Al-11Nb, the achieved powder yield was 80 % after 60 min of discharging, the oxygen pickup was about 0.2 wt.% and the nitrogen pickup about 0.05 wt.% after processing times of 15 h which are in particular remarkable results regarding the affinity of titanium.
In case of the contact material Ag-$Sn0_2$ the dependency of the chemical reaction and the milling temperature has been shown that usable results are not achievable without Cycle Operation.

7. References

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