



## POWDER METALLURGICALLY PRODUCED Ni-35 AT.% AL COMPACTS - A FIRST ASSESSMENT

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### 1. Introduction

The intermetallic phase  $\beta$  NiAl is known to be an alloy with high heat resistance and good oxidation resistance and is being developed as a potential material for high temperature applications (1,2). In addition, off-stoichiometric nickel rich  $\beta$  Ni-Al compositions are known to undergo a thermoelastic martensitic transformation and exhibit shape memory effect at relatively high temperatures (3,4). There is no major difficulty in processing these alloys at elevated temperatures. However, they suffer a major problem of brittle fracture and poor ductility at ambient temperature. In this regard it has been suggested that finer grained NiAl can exhibit enhanced ductility (5,6). Moreover, in quenched alloys containing  $\geq 35\text{at.}\%$  Al there is a problem with reversibility of the martensitic transformation. This is because, martensite decomposes on heating by tempering and this suppresses subsequent transformation to martensite on cooling (7).

Among the new alloy processing practices developed, one of the most attractive is mechanical alloying (MA), which involves repeated welding, fracturing and rewelding of a mixture of powder particles, to produce a controlled, extremely fine microstructure (8,9). The possibility of making nanometer-scale grains using MA, in the case of Ni-Al high temperature and shape memory alloys (SMA) and improving their deformability and near net shaping would thus be of fundamental as well as practical interest.

An important aspect in these studies is the compaction behavior of the MA powder. Powders prepared by MA are generally of equiaxed morphology and can flow to relatively high loose packing densities. Consolidation and pressureless sintering of the MA powder is not feasible because the powder particles are too hard and the green density is lower than that achieved with metal particles. This lower density is partly because the milling process may leave imperfectly packed layers within a powder particle itself.

The aim of this work was to investigate the possibility of producing nickel rich Ni-Al alloys by P/M route. It will also be shown that the tendency for martensite to temper is suppressed with such a method of preparation.

### 2. Experimental

The starting material for this investigation, obtained from X-FORM Co., U.S.A., was reactive sintered intermetallic powder of 65at% Ni - 35at% Al composition with a particle size of about  $45\mu\text{m}$ . This powder was milled in a Retsch model PM4 planetary ball mill or in a Szegvari model 1S attritor.

Batches with different rotation speeds, different ball to powder ratios and milling time were prepared. Table 1 shows the milling parameters which were used. The powder before and after milling was examined by x-ray diffraction, optical and electron microscopy and studied by DSC.

The as received as well as milled material was sintered in vacuum (about  $5 \times 10^{-3}$  Pa) at  $1100^\circ\text{C}$  and 40 MPa pressure in a Gleeble 1500. Before mounting the specimen in the Gleeble, the powder was cold pressed and the resulting compact inserted into a stainless steel tube. A thermocouple was welded to this stainless steel tube. The specimen and graphite stamps were then carefully positioned in the Gleeble (fig.1).

The sintering was performed under high vacuum conditions to prevent oxidation of the powder. The specimen was maintained under vacuum (about  $10^{-3}$  Pa) for at least 20 minutes before starting the sintering. The sintering schedule schematised in fig.2 consisted of gradual heating to  $500^\circ\text{C}$ , holding at this temperature for 10 min for degassing of lubricants, followed by gradual heating again to  $1100^\circ\text{C}$  and compression (to 40 MPa) at this temperature.

The quality of the sintered powder was inspected by examination of microstructures and the measurement of macrohardness. The sintered material was then further annealed for 1 h at  $1250^\circ\text{C}$  under a vacuum of  $10^{-3}$  Pa in a carbolite furnace and subsequently quenched into water at room temperature. This quenched material was characterized by x-ray diffraction ( $\text{CoK}\alpha$  radiation), optical and electron microscopy and tested for martensitic transformation by DSC (using heating and cooling rate  $10^\circ\text{C}/\text{min}$ ).

TABLE 1. Milling Parameters

|                     | Milling media       | Ball to powder ratio | Rotation speed [RPM] | Milling time [h] | Milling atmosphere | Process control agent |
|---------------------|---------------------|----------------------|----------------------|------------------|--------------------|-----------------------|
| Planetary ball mill | steel balls $1/4''$ | 10:1                 | 300                  | 40               | argon              | 1% stearic acid       |
| Attritor            | steel balls $1/4''$ | 50:1                 | 400                  | 80               | flowing argon      | 1% stearic acid       |

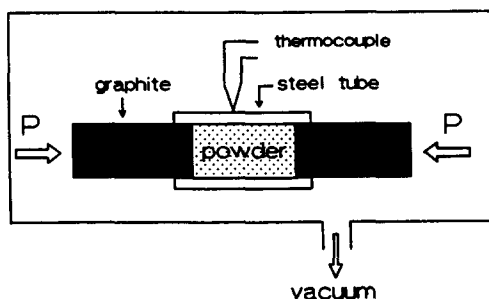


Fig. 1. Steel tube with powder mounted in the Gleeble

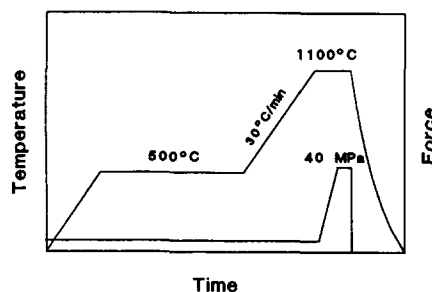


Fig. 2. A schematic diagram representing the sintering process.

### 3. Results

#### 3.1. Powder characterization

Investigation of the powders by optical and scanning electron microscopy showed that mechanical milling changes the size, shape and surface morphology of the powder particles. XRD of as received powder revealed several peaks which could be attributed to the coexistence of three phases -  $\beta$ (NiAl),  $\gamma$ ( $\text{Ni}_3\text{Al}$ ) and  $\text{Ni}_5\text{Al}_3$ . With milling, the intensity of these peaks decreased progressively till finally a single broad peak was left as can be seen in Fig.3. Upon examination of the thermal stability of the milled powder by heating in the DSC, an exothermic reaction was noted as shown in fig.4. Absence of this

transformation on repeated thermal cycling of the same sample established this exothermic reaction to be irreversible.

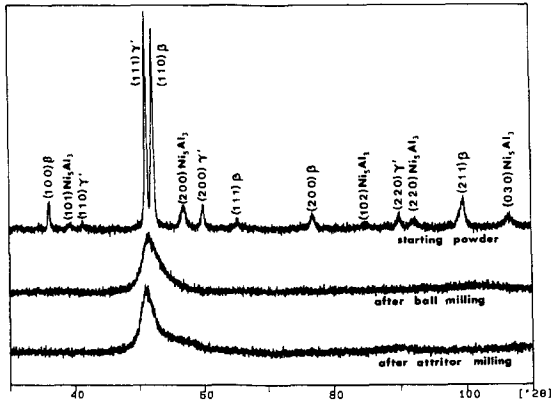


Fig. 3. X-ray diffraction patterns of the powders

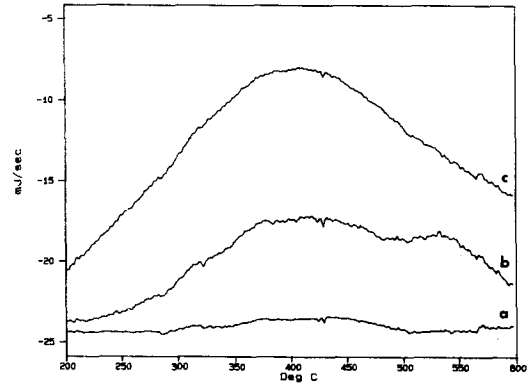


Fig. 4. DSC curves of a) starting powder, b) after ball and c) attritor milling

### 3.2. As received powder - sintered

Non-etched samples studied by optical microscopy revealed the presence of considerable porosity and voids. Estimated sample density was about 89%. The low hardness (fig.5) measured on the same samples could also be attributed to the interconnected pores and large grains (20-50  $\mu\text{m}$ ). Analysis of the XRD data at this stage indicated the presence of  $\beta$ ,  $\gamma'$  and 3R martensite phases.

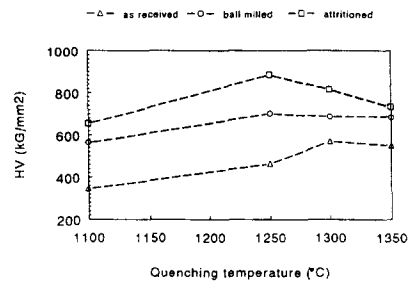


Fig. 5. Macrohardness of sintered compacts

### 3.3. As milled powder - sintered

A high density (as estimated >96%) material was obtained on sintering both the ball as well as the attritor milled powder. XRD results again gave evidence to the presence of  $\beta$  and  $\gamma'$  phases. No martensite phase could be detected in these samples.

### 3.4. Sintered compact - annealed and quenched

Compacts obtained from the as received powder, after annealing and quenching, exhibited in optical microscopy, a relatively large grained (20-50  $\mu\text{m}$ ) microstructure. The interior of each grain had transformed totally to martensite (fig.6a). This was also confirmed by the XRD results, an example of which is shown in fig.7a. Further analysis of the martensite microstructure by transmission electron microscopy (TEM) showed the martensite plates to be finely twinned.

The optical microstructure of annealed and quenched compacts obtained from the ball milled powder, was too fine to distinguish the phases (fig.6b). A representative XRD data of these compacts is shown

in fig.7b. The presence of martensite and  $\beta$  phases is evident from these results and the presence of some  $\gamma'$  phase can still not be ruled out.

Transmission electron microscopy of the samples confirmed the microstructure to be mostly martensitic. The  $\beta$  to martensite transformation had occurred in most cases within fine grains ( $\sim 3\mu\text{m}$ ). In few cases, larger plates of martensite as would occur in larger  $\beta$  grains could also be detected.

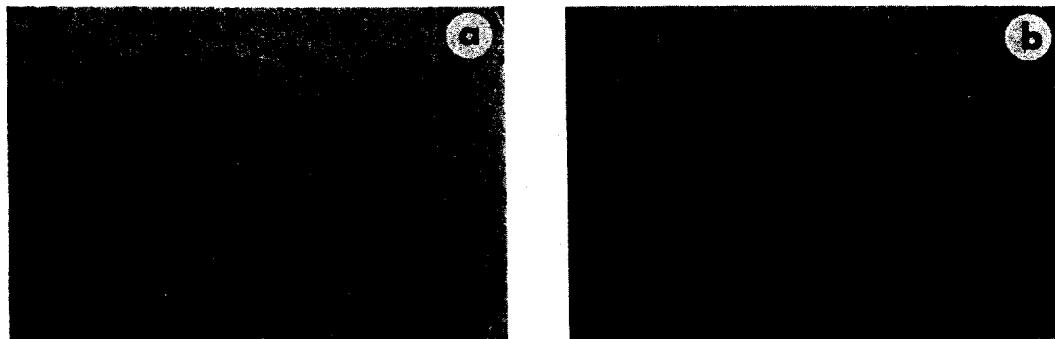


Fig. 6. Optical micrographs of heat treated compacts from a) as received and b) milled powder

Annealed and quenched compacts obtained from attritor milled material also exhibited a fine scale microstructure. XRD analysis indicated the phases present in the material as only  $\beta$  and  $\gamma'$  (fig.7c). Transmission electron microscopy also confirmed the absence of martensite in these samples. Also the microstructure was finer (grain size  $\sim 200\text{nm}$ ) than that observed in the compact from the ball milled powder. Iron contamination ( $<2\%$ ) in the samples could be detected from an x-ray analysis in the SEM. No such contamination was evident, however, upon a similar analysis of the compact obtained from the ball milled powder.

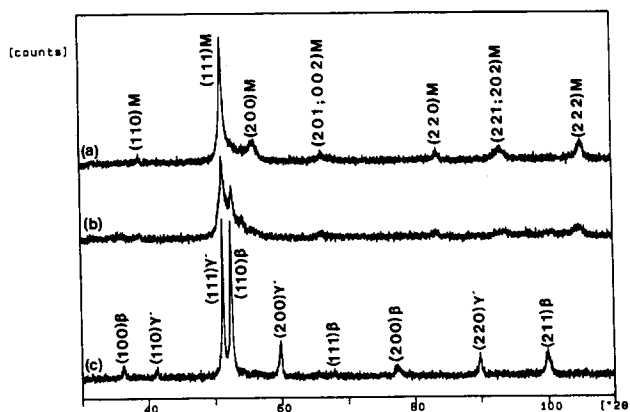


Fig. 7. X-ray diffraction patterns of heat treated compacts from a) as received, b) ball milled and c) attritor milled powder.

Annealed and quenched compacts obtained from the ball milled as well as attritor milled powders exhibited the presence of alumina particles (size 10 - 80 nm). These were found more often in the attritor milled material as compared to the ball milled material. The hardness of the compacts from the milled powders was found to be higher than that reported above for the as received sintered powder. The reason for this could be the presence, as just mentioned, of oxides in the milled powders.

### 3.5. Transformation in sintered compacts as studied by DSC

The DSC results on samples described in sections 3.2 to 3.4 are presented in fig.8. Peaks due to

reversible martensitic transformation are observed in many cases in the 100-300°C range. Besides this, another reversible transformation may also be observed in the range 550-620°C. In the case of annealed and quenched compact obtained from the as received powder, the peaks due to the martensitic transformation are clear and sharp, as is to be expected, in a large grain sized material. The same peaks are broad in samples obtained from ball milled powder. This may be caused by the finer  $\beta$  grains in the ball milled material. However, the peaks belonging to the higher temperature transformation are very clear and sharp. Also the  $\beta$ -martensite transformation temperature of 110°C is lower than that reported (7) for bulk material with the same alloy composition.

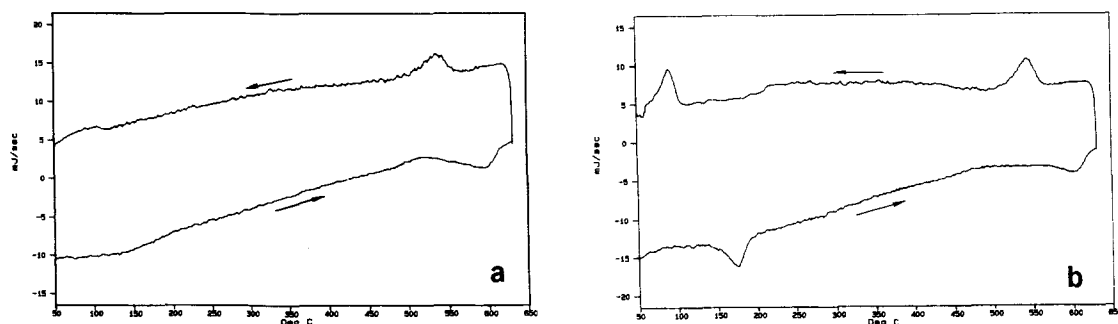


Fig. 8. DSC curves of sintered compact - annealed and quenched obtained from a) as received and b) ball milled powder

#### 4. Discussion

Ball and attritor milling affects significantly the microstructure of powder particles. The peak broadening observed in the XRD spectra after mechanical milling is believed to be mainly due to grain size refinement, strain accumulated in the particle and defects. All these changes together with destruction of chemical order have been considered to contribute to the overall disordering by milling. The exothermic process observed on heating the milled powder in the DSC has thus been considered (10) as an ordering process.

Not only do the powder particles become small and homogeneous after milling but they also become harder and their internal structure changes. The microstructure of the sintered compacts has, therefore, a close relation to the powder preparation method. Besides, the observed maximum energies stored after mechanical milling are large and these contribute to the driving force in subsequent diffusion during sintering. These considerations together with the observed facts such as less porosity and high density, provide the reasons for the better sinterability and the more refined and homogeneous microstructure of the compacts from the ball and attritor milled powders when compared to the as received powder.

No martensite phase has been detected in attritor milled samples. This could be due to several factors such as a lower Ni content in the  $\beta$  phase, a smaller grain size, larger quantity of oxides and defects. The martensitic transformation in this system is thermoelastic in nature. The presence of oxides and defects would increase the non-chemical free energy contribution to the thermoelastic equilibrium (11). For a transformation to be observed at all, this would have to be compensated by the chemical free energy contribution of the thermoelastic equilibrium. This generally requires cooling down to lower temperatures, that results in suppression of the transformation. In this respect non-observance of a transformation would be an indication of the dominance of the non-chemical free energy contribution that cannot be sufficiently compensated by the chemical free energy contribution.

The sintered powder compacts, on heating and cooling, exhibit a reversible martensitic transformation.

Martensite, in a material of the same composition prepared by melting and casting and quenched from the same temperature as the sintered compacts decomposes on heating by tempering to form  $\text{Ni}_3\text{Al}$ . This suppresses subsequent transformation to martensite on cooling. Enhanced diffusion in the presence of quenched vacancies may contribute to such tempering. On the other hand, the absence of tempering in the sintered compacts may be due to the relatively slower diffusion in such material compared to that in the melted and cast material. This could in turn be due to the much finer grain size  $\leq 50\mu\text{m}$  and the presence of fine oxides in the sintered compacts which could serve as effective sinks for quenched in defects. Alternatively, the absence of tempering in sintered compacts may be related to the occurrence of the reversible transformation in the  $550\text{-}620^\circ\text{C}$  range. Further studies are in progress to resolve this issue.

Both the as received and ball milled powders, after sintering, annealing and quenching exhibit a reversible martensitic transformation. Of these, the ball milled powder compacts would be more useable as they are less porous and more dense.

### 5. Conclusions

Nickel rich Ni-Al intermetallic powder can be sintered in Gleeble 1500. The grain size achieved after sintering a milled powder is much smaller ( $<3\mu\text{m}$ ) than that obtained either by conventional melting-casting and processing route ( $\sim 1\text{mm}$ ) or by sintering the as received (reactive sintered) powder ( $30\text{-}50\mu\text{m}$ ). The sinterability of the milled powder is much better than that of the unmilled powder. It is possible to obtain almost fully dense compacts with milled powder.

The sintered powder compacts, from both the as received as well as the ball milled powder, exhibit a reversible martensitic transformation without the hindrance of any tempering leading to  $\text{Ni}_3\text{Al}$  formation. Nevertheless, the compacts from the ball milled material are to be preferred as they are less porous and more dense material. The reversibility of the martensitic transformation may be related to the fine grain size or to another reversible transformation occurring in the range  $550\text{-}620^\circ\text{C}$ .

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