



## ORDERING VERSUS DISORDERING TENDENCIES IN MECHANICALLY ALLOYED $(\text{Ni}_x\text{Fe}_{1-x})\text{Al}$ ALLOYS

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### 1. Introduction

For several years mechanical alloying (MA) and high-energy mechanical milling (MM) have been known to be a promising route for the processing of structural intermetallics such as iron-, nickel- and titanium-aluminides [1,2]. After Ivanov et al. first reported the synthesis of NiAl by MA [3] some research was done to clarify the processes taking place during MA of this and other compounds [4], [5].

The disordering of intermetallic phases by MM has been investigated extensively. Complete disordering of  $\text{Ni}_3\text{Al}$  by mechanical milling was observed by Jang and Koch [6]. Hellstern et al. studied the changes in the structural properties of RuAl with milling time [7] and reported partial disordering of this compound upon milling. Seki et al. investigated disordering of CuTi [8]. Disordering of the CsCl-type compound CoGa was reported by Di et al. [9].

In order to study the factors influencing the degree of long-range order (LRO) established upon MA,  $(\text{Ni}_x\text{Fe}_{1-x})\text{Al}$  alloys were examined by powder x-ray diffraction.

### 2. Experimental

$(\text{Ni}_x\text{Fe}_{1-x})\text{Al}$  ( $x=0\dots 1$ ) alloys were prepared by mechanical alloying of elemental powder blends and for  $x=0$  and 1 by mechanical milling of prealloyed powders under an argon atmosphere. A planetary ball mill (Fritsch pulverisette) was operated at milling intensity 5 (rotation speed 170rpm). The ball to powder weight ratio was 13:1. The particle sizes of the starting powders for mechanical alloying were about 250  $\mu\text{m}$  for Ni and below 44  $\mu\text{m}$  for aluminum and iron. The master alloys for mechanical milling were prepared in an arc melting furnace in an argon atmosphere and crushed to a rather coarse powder (<1mm). The powders were loaded into stainless steel containers in a glove box in a purified argon-atmosphere (<5ppm oxygen). The milling products were characterized by x-ray diffractometry (Siemens D500). Integrated intensities were determined by applying a least squares fit to the data. Grain sizes and internal strains were determined by means of the Debey-Scherrer and Williamson-Hall [10] methods, respectively. Long-time annealing (20h, 1050°C) of as-milled powder samples was carried out under vacuum. The samples were subsequently cooled to room temperature within one hour.

The oxygen impurity level in the milling products was lower than 0.5wt%.

### 3. Results

Figure 1 shows the diffraction patterns of the  $(\text{Ni}_x\text{Fe}_{1-x})\text{Al}$  ( $x=0 \dots 1$ ) alloys milled for 100h. In all cases highly strained ( $\langle \epsilon^2 \rangle^{1/2} \approx 1\%$ ) single phase alloys with bcc structures and nanometer sized crystals were formed. From Fig.1 it can be seen that with increasing the Ni content the degree of long-range order (LRO) increases as is revealed by the increasing intensity of the (100) superstructure peak with respect to the (110) peak. To examine the degree of order more quantitatively, the long-range order parameter  $S$  has been determined in the usual way by referring the intensity ratio  $I(100)/I(110)$  of the as milled samples to that of the completely ordered samples ( $I_0(100)/I_0(110)$ ) which were prepared by long-time annealing.

In Fig. 2 the order parameter  $S$  is plotted against the composition. NiAl exhibits an almost completely ordered structure (B2 type). With increasing iron content,  $S$  decreases continuously to  $S=0$  for FeAl. Within the scatter of the data the dependency of  $S$  on  $x$  appears to be linear.

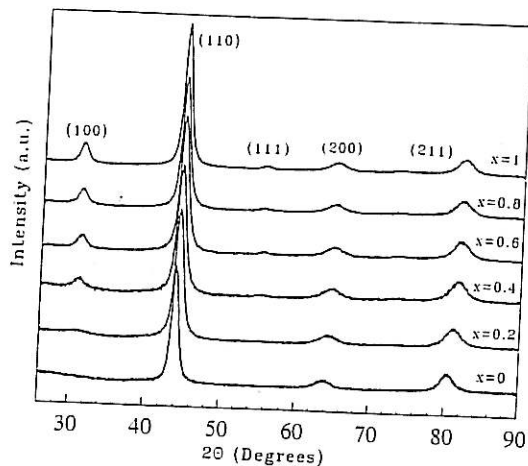


Fig.1 x-ray diffraction patterns of  $(\text{Ni}_x\text{Fe}_{1-x})\text{Al}$  after mechanical alloying (100h/int.5)

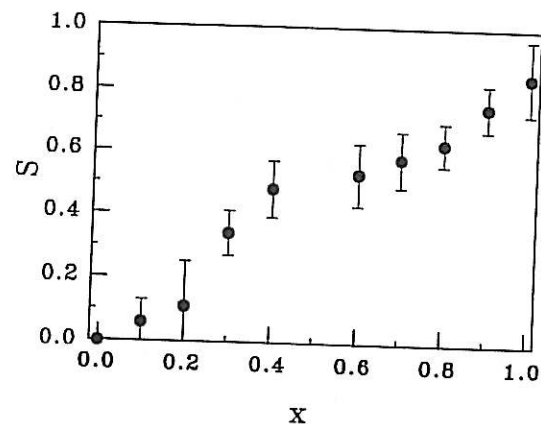


Fig.2: LRO parameter  $S$  for  $(\text{Ni}_x\text{Fe}_{1-x})\text{Al}$  after mechanical alloying (100h/int.5)

In Fig.3 the steady state crystallite sizes, as determined by the Debye-Scherrer formula, are plotted against the composition. There is a minimum in crystallite size in the intermediate composition range which points to an effect of solid solution hardening of the matrix phase (FeAl or NiAl respectively) by increasing contents of the third element. In Ref. [11] a model is proposed which correlates the achievable minimum grain size to the reciprocal hardness in agreement with our experimental observations.

Figure 4 shows the lattice parameters of the alloys both in the as milled and annealed state. After annealing, the lattice parameters for FeAl ( $a_0 = 0.2906(3)\text{nm}$ ) and NiAl ( $a_0 = 0.2886(3)\text{nm}$ ) agree well with literature data ( $a_0 = 0.2903\text{nm}$  for FeAl [12] and  $a_0 = 0.2887\text{nm}$  for NiAl [13]) which indicates near stoichiometric compositions for the milled powders. Obviously, disordering leads to increased lattice parameters in the iron rich alloys which points to the formation of substitutional defects, i.e. antisite disordering. In the case of NiAl, a decrease in lattice parameter upon milling indicates the introduction of triple defects. This decrease in the lattice parameter is readily seen in the inlay of Fig.4, where the lattice parameter of mechanically milled NiAl is plotted against the milling time. After about 40

minutes of mechanical milling, a steady state value of  $a_0 = 0.2878(3)\text{nm}$  is reached which is significantly lower than that of the annealed powder.

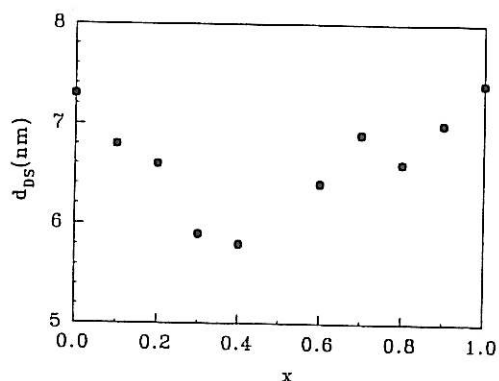


Fig.3: Grain sizes  $d_{DS}$  of  $(\text{Ni}_x\text{Fe}_{1-x})\text{Al}$  as determined by the Debye-Scherrer method after MA (100h/int.5)

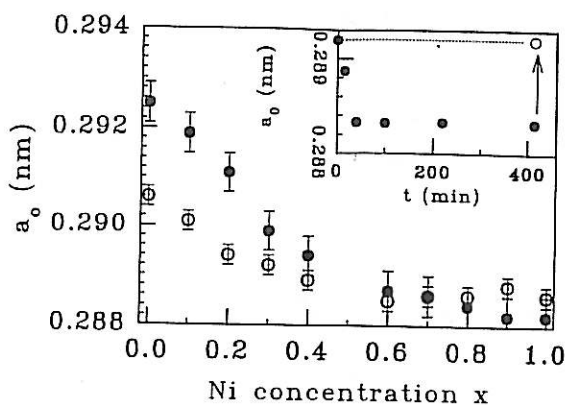


Fig.4: Lattice parameter of  $(\text{Ni}_x\text{Fe}_{1-x})\text{Al}$  after MA (filled circles) (100h/int.5) and after annealing of the MA powders (open circles) ( $1050^\circ\text{C}/20\text{h}$ ). Inlay: Lattice parameter of mechanically milled NiAl as a function of milling time (filled circles). Dotted line: literature data for NiAl. Open circle: lattice parameter of mechanically milled powder after annealing.

In Fig.5, x-ray diffraction patterns of mechanically milled NiAl and FeAl are shown. Mechanical milling of the ordered FeAl master alloys leads to complete disordering, whereas only a small decrease in S was observed for mechanically milled NiAl. Also, the steady state grain sizes and internal strains of the mechanically milled powders are the same as those of the mechanically alloyed samples. Hence, mechanical alloying and mechanical milling of NiAl and FeAl lead to the same final products. Table 1 gives an overview of the finally established grain sizes and internal strains for FeAl and NiAl after mechanical milling and mechanical alloying.

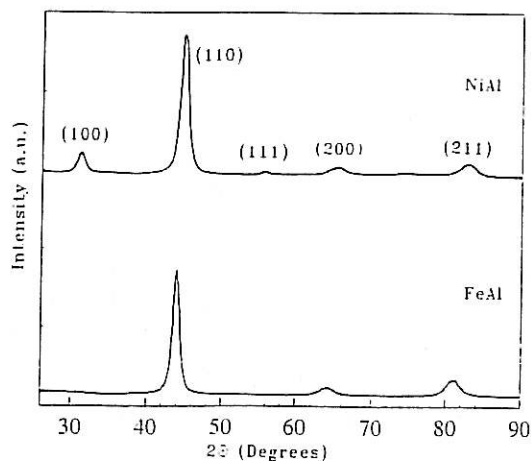


Fig.5: x-ray diffraction patterns of NiAl and FeAl after mechanical milling (50h/int.5)

#### 4. Discussion

The degree of long-range order of mechanically alloyed powders is determined by two competing processes: i.) Thermally activated reordering due to heating up of the milling tools. The influence of increased ambient temperatures on the LRO parameter was recently shown for mechanically alloyed FeAl [14]. ii.) Introduction of atomic disorder by mechanical deformation during milling, e.g., by the creation of antiphase boundaries, complex stacking faults, interstitials, substitutional defects, etc.

Reordering during MA and mechanical milling is driven by the difference,  $\Delta H_{\text{Ord}}$ , in energy between ordered and disordered states. Table 2 shows the enthalpies of formation of NiAl and FeAl. The ordering energy can be estimated from the enthalpies of formation according to the Bragg-Williams theory [15] ( $\Delta H_{\text{Ord}} \approx 0.5\Delta H_f$ ). According to that, FeAl has a much lower ordering energy and therefore the tendency for reordering during MA or MM should be lower.

On the other hand, by assuming that the difference in free energy between the disordered and ordered states shows the same behavior as the ordering energy -i.e., it increases with decreasing iron content- it should be easier to disorder the iron rich alloys: If the free energy of the ordered structure is increased over that of the disordered structure by the introduction of defects, the latter becomes metastable. With the difference in free energy between ordered and disordered state being smaller for FeAl, the transformation to the disordered state should be easier. Brimhall et al. [16] report on ion irradiation experiments on FeAl and NiAl. In both cases a highly ordered structure was maintained upon radiation at near ambient temperatures. According to them a critical defect density is needed for the formation of metastable phases. Obviously in their irradiation experiments this critical defect density was not reached, leaving FeAl and NiAl in an ordered state. Ball milling results in disordered FeAl, indicating a higher defect density and /or different kinds of defects. Moreover, one of the major differences in the deformation-mechanisms of NiAl and FeAl lies in the number of slip systems. Only three  $\langle 100 \rangle \{ 110 \}$  slip systems are frequently observed in NiAl [18], whereas for FeAl additional  $\langle 111 \rangle \{ 110 \}$  slip is found [17,18].  $\langle 111 \rangle \{ 110 \}$  slip in FeAl is associated with the creation of antiphase boundaries and represents an additional way of introducing disorder into the crystal lattice.

The assumption of a significant influence of the mechanical properties on the finally established LRO parameter is consistent with the results of Hellstern et al.. The authors mechanically milled RuAl (B2 structure) and reported partial disordering of this compound [7]. They found a value of  $S \approx 0.5$  (their slightly different definition for  $S$  is taken into account). Although no experimental data on the enthalpy of formation of RuAl are available, there are calculations by W.Lin et al. [21] who report a value of 75 kJ/mol (their calculated value for NiAl agrees well with experimental results). According to this, NiAl and RuAl have almost the same enthalpy of formation but different degrees of LRO after intensive mechanical milling, a fact that can be attributed to the different deformation mechanisms of RuAl and NiAl. Like FeAl, RuAl shows  $\langle 111 \rangle \{ 110 \}$  slip [22]. Unfortunately, on the basis of our experiments, it is not possible to separate the contributions of the mechanical properties and the different ordering energies to  $S$ . Eridon et al. [17] have pointed out the influence of both thermodynamics (ordering energy) and kinetics (thermally activated reordering) on the phases formed during ion-beam mixing in the Ni/Al system.

According to Hellstern et al. [7] a large contribution to disordering should arise from grain refinement upon MA or MM. They argue that one monolayer of atoms near the grain boundary should not participate in LRO and thus cause a grain size dependent reduction in S. This reduction in S should increase with decreasing grain size as the number of atoms in the grain boundary increases with respect to the total number of atoms in the grain. This result is not consistent to our results, as the grain size and hence the number of atoms near the grain boundary is approximately the same for NiAl and FeAl, whereas the values for S are completely different.

The fact that the grain sizes determined from the peak widths of the (100)-superlattice reflection and the (110) reflection are almost identical indicates that disordering occurs throughout the whole grain. A sub-structure of ordered domains within each grain would cause enhanced broadening of the superstructure-peaks with respect to the normal peaks.

### 5. Conclusions

(Ni<sub>x</sub>Fe<sub>1-x</sub>)Al alloys (x=0...1) were prepared by mechanical alloying of elemental powders and by intensive mechanical milling of master alloys for x=0 and 1. Both mechanical-milling and mechanical alloying result in single phase alloy powders with highly strained nanometer sized crystals. The degree of long-range order after milling was found to vary with composition x. NiAl exhibited an almost completely ordered structure (B2-type). With increasing Fe content, the LRO parameter S drops continuously to S=0 for FeAl. This difference in LRO is attributed to:

- i.) enhanced thermally activated reordering of the Ni-rich alloys during milling driven by the high ordering energy of these alloys
- ii.) enhanced disordering of the Fe-rich alloys by the introduction of defects due to a smaller difference in free energy between ordered and disordered state.
- iii) enhanced disordering of the Fe-rich alloys due to different deformation mechanisms with respect to NiAl.

The lattice parameter of disordered FeAl was found to be higher than that of ordered FeAl, which indicates the formation of substitutional defects by disordering. In contrast, mechanical alloying of NiAl leads to decreased lattice parameters, probably caused by the formation of triple defects.

	NiAl (MM)	NiAl (MA)	FeAl (MM)	FeAl (MA)
$\langle \epsilon^2 \rangle^{1/2}$ (%)	1.1	1.2	2.4	2.4
D (nm)	13	9	7	8

Table 1: Grain sizes D and internal strains  $\epsilon$  of NiAl and FeAl after mechanical alloying (MA) and mechanical milling (MM)

	$\Delta H_f$ (kJ/mol)	S
NiAl	72	0.8±0.1
RuAl	75	0.5*
FeAl	25	0

Table 2: Enthalpies of formation for NiAl and FeAl according to [13] and of RuAl according to [19]. \* was taken from Ref. [7]. LRO parameter S after intensive mechanical milling.

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