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Compositional Analysis of Ni-Zr Powder during Amorphization by Mechanical Alloying.

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Abstract. – We prepared amorphous Ni-Zr powder by mechanical alloying. The solid-state amorphization reaction is monitored by X-ray diffraction, SEM and microprobe analysis. During the milling a layered structure of the crystalline elements develops. At the boundaries the amorphous alloy is formed by interdiffusion. The layers of the crystalline elements become thinner and the amorphous parts grow when the alloying period is increasing. The amorphous parts grow by cold welding of the smaller parts.

Introduction. In a previous paper [1] we reported the preparation of amorphous Ni-Zr powder by mechanical alloying using a ball miller. It turned out that during the alloying the intensity of the Bragg reflections in the X-ray pattern decreases and that a broad peak, characteristic of amorphous alloys, appears. HELLSTERN and SCHULTZ [2] prepared amorphous alloys by the same method and showed in an optical micrograph that after a short milling period a Co-Zr powder particle contains a layered structure. This may indicate a similarity between the solid-state amorphization reaction described above and the one obtained by heating a multilayered structure of pure crystalline films [3]. In the present paper we will report on the structure and compositional analysis of Ni-Zr powder by scanning electron microscopy and electron microprobe analysis during the amorphization by mechanical alloying.

Experimental procedures. A mixture of nickel and zirconium powders with a nominal composition of 62 at% Ni were mixed in a glove box under purified argon. The total mass of the powder was about 0.6 g. The milling was carried out in a steel cylindrical vial with a tungsten-carbide bottom. One hardened steel ball with a diameter of 6 cm was used. The ball was kept in motion by mounting the vial on a vibrating frame. To avoid oxidation, the alloying was carried out under an argon flow.
X-ray diffraction patterns were taken by means of a vertical powder diffractometer with CuKα radiation.

The compositional analyses were performed on a Jeal 747 Superprobe at the Eindhoven University of Technology, using the matrix correction program developed by BASTIN [4, 5].

**Results and discussion.** X-ray diffraction and electron microprobe analysis were performed on the Ni-Zr powder after several milling periods. Figure 1 shows the diffraction patterns after 4.8, 9, 18, 35.5 and 70 hours of milling. It is clearly visible that the intensity of the Bragg reflections decreases and that the broad peak of the amorphous alloy appears during the alloying. (The peaks seen in the X-ray patterns after 70 hours of alloying are...
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Fig. 2. - BSI of a polished Ni-Zr powder particle after 4.8 hours of milling.

Fig. 3. - BSI of a polished Ni-Zr powder particle after 9 hours of milling.

tungsten carbide impurities from the bottom of the vial.) The same samples were also studied by electron microscopy and electron microprobe analysis.

Figure 2 shows a SEM back-scattered electron image (BSI) of a polished powder particle after 4.8 hours of milling. With microprobe analysis it is found that the dark parts in this BSI are Ni-rich and the white parts are Zr-rich, while the grey parts are alloyed Ni-Zr. Table I gives the averaged composition of 1 μm³ around several points. From the large dark parts it can be seen that the powder particle in fig. 2 has large Ni areas. Some of them are oval-shaped and some layer-shaped with a typical thickness of about 2 μm. For the white Zr-rich parts a layered structure is also visible. The grey parts, consisting of alloyed Ni-Zr have a layered structure with a layer thickness of about (1±2) μm. The alloyed Ni-Zr parts are very thick compared to a reasonable diffusion length in an amorphous alloy. If, for example, it is supposed that the local temperature during the milling is 500 K, so that a diffusion coefficient is about 10⁻¹⁷ cm²/s [6], the diffusion length after 4.8 hours is 60 Å. From this it can be concluded that during the milling a continuous deformation and cold welding take place, and this rather than that diffusion is responsible for the alloying. Other powder particles after 4.8 hours of milling show the same kind of structure as the particle shown. Particles with large Zr areas were also found.

Figure 3 shows a BSI of a powder particle after 9 hours of milling. The layered structure with Ni-rich, Zr-rich and alloyed Ni-Zr are clearly visible. The typical layer thickness is around 1 μm. Table II presents the average composition of 1 μm³ around the given points. It is clear that the layers are thinner and the fraction of alloyed Ni-Zr is higher here than after 4.8 hours of milling. Furthermore, the white Zr-rich parts contain more Ni than those after 4.8 hours of milling, whereas the black Ni-rich parts contain more Zr.

Figure 4 shows a BSI of a powder particle after 18 hours of milling. Here the layer structure is almost lost. The largest average Zr concentration in 1 μm³ is 67 at% and the largest Ni concentration is 67 at%. The layers that are still observable have a thickness about 0.4 μm. The white spots on the micrograph are tungsten carbide impurities that originate from the bottom of the vial.
TABLE I. - Composition of several points in a powder particle after 4.8 h of alloying.

<table>
<thead>
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<th>Composition</th>
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<tbody>
<tr>
<td>1</td>
<td>Ni₉₇Zr₃</td>
</tr>
<tr>
<td>2</td>
<td>Ni₇₈Zr₂₂</td>
</tr>
<tr>
<td>3</td>
<td>Ni₆₀Zr₄₀</td>
</tr>
<tr>
<td>4</td>
<td>Ni₈₉Zr₶₁</td>
</tr>
</tbody>
</table>

TABLE II. - Composition of several points in a powder particle after 9 h of alloying.

<table>
<thead>
<tr>
<th></th>
<th>Composition</th>
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<tbody>
<tr>
<td>1</td>
<td>Ni₃₃Zr₆₇</td>
</tr>
<tr>
<td>2</td>
<td>Ni₆₁Zr₃₉</td>
</tr>
<tr>
<td>3</td>
<td>Ni₄₄Zr₁₆</td>
</tr>
</tbody>
</table>

Figure 5 shows a BSI after 35.5 hours of milling. No layer structure is visible any longer, even at a magnification of 3600 x. The white parts are WC and the black lines are fractures. The Zr-rich parts have a maximum concentration of 46 at% Zr. After 70 hours of milling no concentration gradients were measured. The final composition is Ni₆₀Zr₄₀. The loss of nickel compared to the starting composition of the powder mixture may be explained as due to the blowing away of the powder by the argon flux or to spreading out as a thin film on the ball or the bottom.

Figure 6 shows a plot of the logarithm of the layer thickness vs. the milling time. Linear extrapolation gives a layer thickness of 500 Å after 35.5 hours of milling. This layer thickness is remarkably of the same magnitude as the layer thicknesses used for the solid-state reaction in thin films [3]. This extrapolation to 70 hours of milling gives a layer thickness of 8 Å, which is a few interatomic distances.

Fig. 4. BSI of a polished Ni-Zr powder particle after 18 hours of milling.

Fig. 5. BSI of a polished Ni-Zr powder particle after 35.5 hours of milling.
Fig. 6. – Logarithm of the layer thickness vs. the milling time for Ni-Zr powder.

Conclusions. From the above we conclude that by cold welding and continuous deformation, more or less alternating crystalline layers are formed, that decrease in thickness during the milling processes.

The amorphization of the material occurs during the process by interdiffusion. In this picture the amorphization process is similar to the amorphization in multilayered structures during heating[3]. Apparently amorphous parts grow by cold welding of thin amorphous layers formed by interdiffusion. The eventual homogenization takes place by cold welding combined with further diffusion.

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