Mechanically induced chemical and structural changes in materials
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Chapter 5

Metal-particle sizes in metal/non-metal mixtures

5.1 Introduction

As mechanical milling has long been used as a means for particle size refinement, this is the obvious long-known application of this technique. Renowned appliances are found in the fields of mineralogy and food procession. Dependent on the mechanical properties of the material, mechanical milling may give rise to either larger or smaller particles. For milling treatments in the absence of mechanochemical reactions (discussed in chapter 6), fracture and cold welding of particles are competitive effects. The particle growth rate, that can either be positive or negative, depends mainly on the hardness and ductility of the material, as well as on the free surface energy. For most common milling treatments, such as in mineralogical winning, brittle ceramic materials are milled (sandstone, limestone, granite), and a negative growth rate explains the evident use of the technique. Pure metals, however, are very ductile materials and have high cohesive energies, which will generally result in a positive growth rate. Hardness and ductility depend on the temperature at which milling is carried out (cf. also chapter 3) and under appropriate conditions, e.g. at sufficiently high temperatures, formation of a metal slab will occur. However, by adding a medium to a metal powder, the particle growth rate generally decreases. It is assumed that breaking of the metal particles will still occur while frequent contact between the particles and thus coagulation due to cold welding is avoided.

Particle-growth behaviour of metal powders in various milling environments is investigated in this chapter. The milling medium may not only influence the particle size due to the spacing that is introduced between the metal particles, but also by interaction with the metal. In the latter case, interaction is determined by the difference between free surface energy of the metal and adhesion energy between metal and medium, and also by the possible chemical binding energy between metal and medium. We attempt to determine the principal factors that play a role in particle growth during milling of various systems. As small particles may have interesting magnetic and catalytic properties, they may also deserve further research. Therefore, the possibility of the presence of such characteristics of the small metal particles is also investigated.

In mechanically milled immiscible mixtures of metals, both undercooling and superheating of small particles in a metallic matrix have been observed. A well-defined orien-
tation relationship between the small metal particles and the matrix of the bulk medium may induce superheating of the particles, as has been demonstrated for Pb embedded in Al, Cu and Ni matrices after rapid solidification [1]. After repeated thermal cycling, defects in the form of steps are introduced and weaken the metal/matrix orientation relation. Consequently, the superheating behaviour is drastically reduced, as shown in the case of Pb in Cu-Zn matrices [2]. In contrast to quench-cooled ribbons, random orientation is found in ball-milled mixtures and no superheating is observed [3]. Instead, melting endotherms with lower onset temperatures are observed, as well as large undercooling of the nanoparticles during cooling for In, Sn, Bi, Cd and Pb in Al [4]. Both melting-point depression and reduction of heat of fusion were observed to be inversely proportional to the size of the embedded particles. The melting-point depression \((T_m - T_m^0)\) with respect to the bulk melting temperature \(T_m^0\) could be described by the relation

\[
\frac{T_m}{T_m^0} = 1 - \frac{6(\sigma_{sm} - \sigma_{lm})}{\rho H_m^0 d}
\]

with \(\sigma_{sm}\) and \(\sigma_{lm}\) the interface energies of solid particle-matrix and liquid particle-matrix, \(H_m^0\) the latent heat of fusion, \(d\) the particle diameter and \(\rho = (\rho_s + \rho_l)/2\), with \(\rho_s\) and \(\rho_l\) the densities of the solid and liquid particles. The melting enthalpy \(H_m\) with respect to the bulk latent heat of fusion \(H_m^0\) could be described by

\[
\frac{H_m}{H_m^0} = 1 - \frac{6\delta(H_m^0 - H_m^{int})}{H_m^0 d}
\]

with \(H_m^{int}\) the melting enthalpy of the interface layer and \(\delta\) the thickness of the interface layer. Melting-point depression and reduction of heat of fusion were thus found to depend on the excess enthalpy of the particle/matrix interface and on the (positive) heat of mixing. In general, nucleation and growth rate determine the freezing temperature as well as the average crystallite size during cooling. The large undercoolings were found to result from the energy barrier for solid nucleation and a relation was observed with the size dependence of the melting point. Investigation of melting and freezing may thus assist in characterisation of metal particles in metal/medium mixtures.

Very few studies exist of mechanically milled mixtures of metals and non-metals. In Fe/high-density polyethylene (HDPE) mixtures, nanosized Fe crystallites have been observed with enhanced coercivity, attributed to the presence of single-domain particles (<15 nm) in the sample [5]. Similar effects were found in mixtures with ceramics, such as α-Al₂O₃ [6], SiO₂ [7] and ZrO₂ [8]. Coercivities of the same order had been observed for samples that had been prepared by sputtering. Cu/HDPE mixtures showed the formation of electrically conductive samples due to the presence of flake-like Cu particles that increase conductivity, while amorphisation of PE occurs for large volume fractions (50%) of Cu [9]. Enhanced conductivities were also found for Al/poly(methyl methacrylate) (PMMA) mixtures [10], although large volume fractions of Al were required for the formation of continuous chain-like agglomerates of Al responsible for conductivity. Flake-like structures of both metal and polymer have also been observed in Cu/polytetrafluoroethylene (PTFE) and Ni/PTFE mixtures [11]. For metal fractions of 32 vol.%, amorphisation of PTFE was observed, while formation of NiF₂ indicated that decomposition of the polymer had occurred.
In this chapter, we explore several systems in which a metal is mixed with a non-metallic medium. A number of Ni samples are compared after milling at room temperature and at 77 K as well as in a rubber polymer. In this way, particle growth is considered as a function of milling temperature and some specific particle morphologies are encountered. Milling of Cu in a number of environments, notably vacuum, ethanol, glycerol, Al₂O₃ and a number of different polymers, is carried out in order to assess the influence of the milling medium on the particle and crystallite sizes. Finally, by milling one of these polymers, polybenzimidazole, together with In and Bi and investigation of the melting behaviour of these metals, the relation between metal particle size distribution and melting behaviour is studied. Structure formulas of the polymers can be found in figure 4.1 and figure 5.1. In order to avoid reactions with oxygen or nitrogen, milling was always carried out in the vibratory mill either under vacuum or in an inert atmosphere.

5.2 Milled Ni and Ni/rubber mixtures

In order to probe the effect of temperature on the particle size of Ni, 3 g of Ni (≤44 μm, 99.9% pure, purchased from CERAC) was milled under vacuum at room temperature, as well as at 77 K by cooling with liquid N₂. By means of light microscopy, most particles were observed to have sizes of about 0.03 mm prior to milling. After 50 h of milling, large particles had been formed at room temperature, with particle diameters within a small range between 0.3 and 0.5 mm. At 77 K, significant broadening of the particle-size distribution was observed, with particle diameters between 0.01 and 0.1 mm. The average particle size had increased slightly to between 0.04 and 0.06 mm. Ni particles had formed alloys with the milling vial, making this material not an ideal probe for milling. By means of X-ray analysis, line broadening could be observed, and average crystallite sizes were determined of 13 nm for both milled Ni samples, in contrast to large sizes (≥50 nm) for the unmilled material. Some orientation effects could be observed, as the (111) reflections indicated crystallite sizes of 20 nm.

In order to study the size distribution and morphology of Ni particles in a rubber polymer, Ni was milled together with polybutadiene (PBD), which is a highly elastic material at room temperature. Fields of applications of this system could be chemically active membranes with metal particles and conductive glutinous polymers. The polymer sample was obtained from Aldrich, consisted of 36% cis, 55% trans and 9% 1,2-addition, and had a molecular mass Mₘₐ of 4.2·10⁵. In order to ensure that no volatile components or air would remain encapsulated in the polymer, PBD was pre-milled during 16 h under vacuum. 0.8 g of Ni was milled together with 2.2 g of PBD (3.5 vol.% of Ni) and samples were taken after 50, 100 and 200 h. A firm metal-coloured slab had been formed, lining
the bottom of the vial. After sample taking, the slab was torn and folded after which milling was continued.

At the outside of the slab, Ni particles of up to 0.05 mm could be observed that had not been able to enter the bulk of the polymer, making the sample quite inhomogeneous. TEM analysis was carried out of samples that were sliced from the inside of the slab with an ultramicrotome under liquid N$_2$. In the inner part of the polymer, a broad size distribution was observed from 50 h on (figure 5.2a), with sizes between 0.02 and 15 $\mu$m. The smallest particles had a needle or disk-like shape, and some folded structures were observed (figure 5.2b), for which the contact between the metal particles was clearly hindered by the presence of PBD. No significant changes in the broad particle-size distribution were observed during milling, and it became clear that the smallest particles were polycrystalline (figure 5.2c). XRD line broadening indicated average crystallite sizes of 25 nm for all milling times. Orientation effects were also prominent in these samples with sizes of 35 nm for the (111) reflections. Milling of a sample consisting of 1.56 g of Ni with 1.44 g of PBD (10 vol.% of Ni) however, resulted in crystallite sizes of the same order as those of the milled pure Ni samples. This was the case both for milling at room temperature and at 77 K.

With fracture and cold welding acting as competitive mechanisms during milling, it has clearly been demonstrated that due to enhanced brittleness at a lower milling temperature cold welding is suppressed, while the probability of fracture remains similar. The latter becomes clear from the equal crystallite sizes at room temperature and at 77 K for identical milling times and amounts of material. The grain size may also be a result of work hardening, which would imply that a minimum grain size has been reached, but this obviously has no consequences for differences in the probability of fracture at
this point. Introduction of spacing on the other hand suppresses cold-welding behaviour and decreases the probability of fracture. The latter may be explained by the lower intensity of milling due to the damping influence of the elastic PBD medium. This is supported by the fact that no further change in crystallite size occurs after longer milling times. Moreover, smaller crystallites are formed in case less PBD is present. Except by smaller average particle sizes, differences appear through the much broader particle-size distribution. As fracture of particles occurs randomly, the particle-size distribution will always become broadened, except in the case of significant cold welding. As both larger particles and a narrower particle-size distribution are observed at 77 K, cold welding is still more prominent at lower temperatures than in the case of introduction of spacing. Deformation of the Ni particles is most prominent for the Ni/PBD mixture. As the particles remain much more fixed in the medium, repeated impacts may result in more deformed particles than in the case particles may also weld together, which clearly occurs without PBD at room temperature. However, orientation effects suggest that similar deformations of the individual crystallites also occur without a medium. Due to cold welding this is not visible in the individual particles.

D.c. hysteresis loops of Ni/PBD samples have been determined by means of a Maglab–Exa magnetometer at 5 K (section 2.3.5). The hysteresis loop for the sample milled during 100 h is shown in figure 5.3a. The maximum applied field was 1 T for all samples, at which saturation was reached. Small differences in the saturation magnetisation between the different milling times can be attributed to inhomogeneities of the samples, giving rise to small variations in the Ni content. For all samples, coercivities of 0.013 T were measured. For remanent magnetisations $M_r$ (as compared to the saturation magnetisations $M_s$),

Figure 5.3: Magnetisation of Ni/PBD mixtures after milling: (a) hysteresis loop (100 h) and (b) temperature dependence at 0.05 T (50 h)
a value $M_r/M_s$ of 0.18 was found after 50 h of milling and a value of 0.20 after 100 h and 200 h. As the remanent magnetisations and coercivities for bulk Ni are negligible, very small particles are confirmed to have been formed during milling with PBD. The high coercivities can be attributed to single-domain particles, similar to those observed in Fe/HDPE [5]. Temperature-dependent d.c.-field measurements, carried out at 0.05 T in a Quantum Design SQUID magnetometer, show differences between zero field-cooled (ZFC) and field-cooled (FC) curves (figure 5.3b). Irregularities in the curves can be attributed to small movements of the sample during the measurement, which are hard to avoid. The differences also indicate the formation of very small particles. Superparamagnetic behaviour of small single-domain Ni particles is suggested, with interactions between the small particles being possibly responsible for differences between FC and ZFC curves. However, grain boundaries in the Ni particles may also be responsible for the differences in FC and ZFC curves, and more careful examination of the system would be required to draw firm conclusions about the magnetisation behaviour. Again, no experimentally significant changes were observed for the various milling times.

No clear application is yet to be expected as, due to the broad particle-size distribution and thus the presence of some very large particles, the bulk properties are predominantly determined by the large particles. Separation of the smaller particles, however, would give interesting possibilities for applications of the magnetic properties.

5.3 Milled mixtures with Cu

In order to assess the influence of the milling medium on the particle size and to reveal possible interactions between metal and medium, milling of Cu has been carried out in a number of different environments. These include liquid and solid mediums and are compared to Cu that has been milled under vacuum. All samples were milled during 50 h. Milling of mixtures of Cu and a solid medium was carried out under vacuum, while mixtures of Cu and liquids were milled in a flow of Ar (purity 99.999%). Cu powder (<44 μm) with a purity of 99.5% was purchased from CERAC. A volume averaged mean particle diameter of 15 μm was determined by means of a Coulter Multisizer.

Liquid mediums that were applied for milling of Cu included ethanol and a mixture of glycerol and ethanol (volume ratio 2:1). Ethanol was added to glycerol in order to decrease the viscosity and thus enable movement of the ball. 2 g of Cu was milled, as in the case of milling under vacuum. Ample liquid was added so that the upper level of the liquid was 2 mm below the top of the ball. For the sample that was milled in ethanol, Cu was mainly found at the bottom of the mill, and the ethanol evaporated quickly from the sample after milling. The sample that had been milled in the glycerol/ethanol mixture remained immersed in the liquid. It took several days of waiting before a liquid layer was again visible above the Cu particles, which indicates that a homogeneous mixture of the metal and the liquid existed during milling. After milling under vacuum, the volume-averaged mean Cu-particle diameter had increased (table 5.1), while no significant broadening of the particle-size distribution had occurred. Milling in ethanol showed no significant change in the mean diameter, whereas milling in the viscous glycerol/ethanol mixture resulted in a much smaller particle size. In both ethanol and glycerol/ethanol, the particle-size distributions were broadened. In the latter case however, the lower
Table 5.1: Cu volume fractions, mean volume-averaged particle diameters (electrical sensing zone), particle-size distributions (solid mediums, TEM) and crystallite sizes for milled Cu mixtures

<table>
<thead>
<tr>
<th>Milling medium</th>
<th>fraction</th>
<th>particle diameter</th>
<th>crystallite size all reflections</th>
<th>crystallite size (111) and (222)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none (unmilled)</td>
<td>100 [vol.%]</td>
<td>15 [µm]</td>
<td>50 [nm]</td>
<td>50 [nm]</td>
</tr>
<tr>
<td>vacuum</td>
<td>100</td>
<td>34</td>
<td>16</td>
<td>21</td>
</tr>
<tr>
<td>ethanol</td>
<td>–</td>
<td>13</td>
<td>18</td>
<td>24</td>
</tr>
<tr>
<td>glycerol/ethanol</td>
<td>–</td>
<td>2.4</td>
<td>16</td>
<td>22</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>12</td>
<td>0.01–0.03</td>
<td>29</td>
<td>42</td>
</tr>
<tr>
<td>HDPE</td>
<td>3.4</td>
<td>0.01–0.3</td>
<td>16</td>
<td>18</td>
</tr>
<tr>
<td>PTFE powder</td>
<td>≥ 7.4</td>
<td>0.02–0.08</td>
<td>39</td>
<td>49</td>
</tr>
<tr>
<td>PTFE flakes</td>
<td>≤ 7.4</td>
<td>0.01–0.06</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>PBI</td>
<td>2.8</td>
<td>0.2–1</td>
<td>29</td>
<td>37</td>
</tr>
</tbody>
</table>

part of the distribution could not be observed due to instrumental restrictions. The fact that only limited sintering of Cu occurs and that no metal slab is formed during milling under vacuum may be attributed to the oxidation layer that is always present on metallic Cu. For this material, the oxidation level is of the order of 5% (section 6.2.2). The surface passivation layer may hinder agglomeration of metal particles as well as enhance brittleness. A decrease of the crystallite size was observed (table 5.1), but no differences could be observed between the samples milled in ethanol, glycerol/ethanol or the sample milled under vacuum. Cold welding has clearly been suppressed in the presence of an organic liquid due to the introduction of spacing, especially in the highly viscous glycerol/ethanol mixture, whereas crystallite-size refinement and consequently the probability of fracture have remained roughly equal. However, orientation effects were found, as less extensive crystallite-size refinement was observed for the (111) and (222) reflections.

For mixtures of Cu with a solid, powders of γ-Al₂O₃, high-density polyethylene (HDPE) and polytetrafluoroethylene (PTFE), 0.5 g of Cu was milled with 1.5 g of the solid medium. A mixture of polybenzimidazole (PBI) and Cu is discussed in section 5.4. Metal-volume fractions are given in table 5.1. The HDPE (Hostalen) and PTFE samples are described in section 4.5 and γ-Al₂O₃ was purchased from Ketjen (type CK300). For HDPE, some flake-like Cu-coloured agglomerations were formed, although the material had remained a powder. As in the case of pure HDPE (section 4.5), a transition from orthorhombic to monoclinic had taken place, while no amorphisation of HDPE could be observed. This transition has not been observed in Fe/HDPE [9], whereas the absence of amorphisation is in line with the observations for similar low metal volume fractions in this paper. For PTFE, the ball was entirely covered with Cu-coloured flakes, while a lighter-coloured powder was found at the bottom of the mill. From X-ray diffraction lines however, slightly more Cu was observed in the powder mixture than in the flakes. The flake-like structure and absence of amorphisation of PTFE for small Cu fractions are in line with observations in ref. [11]. Homogeneous powder mixtures were formed for γ-Al₂O₃ and PBI.
Figure 5.4: TE micrographs of mixtures with Cu after 50 h of milling: (a) Cu/PTFE flakes, (b) Cu/PTFE powders, (c) Cu/HDPE and (d) Cu/γ-Al₂O₃
The metal-particle sizes of the mixtures were determined from TEM measurements on the edges of the powder particles and the flakes. Size distributions are given along with the crystallite sizes in table 5.1. Clearly, the crystallite sizes are larger for the powdered mixtures than for the other milled Cu mixtures (including HDPE and PTFE flakes). Moreover, for the flakes, orientation effects of the crystallites are less prominent. Probably, Cu particles are better embedded in the flakes and thus undergo a more homogeneous and extensive deformation. Spacing of the particles is also better in this way with respect to the mixed powders, which may explain the smaller particle sizes observed in PTFE with respect to PBI. From the TE micrographs, more deformation of the particles is observed however for the PTFE flakes than for the powders (figures 5.4a and b). The TE micrograph of Cu/HDPE (figure 5.4c) also shows the presence of some deformed metal structures. Repeated deformation in the same direction is expected to be responsible for the stretched metal structures observed in the flakes, as was also the case for Ni/PBD mixtures (section 5.2). The extensive deformation undergone may also lead to the formation of very small crystallites. This remarkably does not lead to clear crystallite-orientation effects, which can possibly be caused by the small size of the crystallites. For Cu/γ-Al₂O₃, little contrast was found between Cu and alumina (figure 5.4d), which can be attributed to the high magnification that was needed for investigation of the small particles. Some darker spots can be distinguished, which might be Cu particles with sizes of 10–30 nm. These particles would then be of the same size as the crystallites, although considering the crystallite size it is likely that larger Cu particles are also present in the sample. No relation could be observed between the crystallite sizes and the volume fractions of Cu in the different samples. An explanation that larger crystallites are observed in γ-Al₂O₃ and PBI may be that these materials are harder and more brittle and thus leave less energy available for deformation and fracture of Cu particles (cf. also figure 5.5c).

5.4 Melting-temperature depression and undercooling in metal/polymer mixtures

Comparison of different mixtures of a metal with the same polymer was carried out by milling of mixtures with polybenzimidazole (PBI). PBI is a brittle polymer with superior thermal stability that is applied for high-performance-engineering purposes, and has a glass-transition temperature \( T_g \) of about 425 °C. Besides Cu, of which various mixtures have been described in section 5.3, In and Bi were milled together with PBI. As In and Bi have melting temperatures \( T_m \) below the \( T_g \) of PBI, the melting behaviour of these metals can be studied without affecting the characteristics of the polymer matrix. In this way, the relation with the metal-particle-size distribution can be assessed.

0.2 g of metal powder was milled together with 1 g of PBI (purchased from Aldrich), after pre-milling of PBI during 25 h under vacuum. Blank ‘unmilled’ samples were obtained by mixing In powder (<44 μm, 99.999% pure, CERAC) and Cu with the polymer. Of Bi (99.999% pure, Aldrich), chunks were milled together with the polymer for 1 min, which was sufficient for the highly brittle metal to become powdered and distributed throughout the sample. The results obtained on the In/PBI and Bi/PBI mixtures are given in table 5.2 while some structural data for the Cu/PBI mixture have been included.
Table 5.2: Metal-volume fractions, particle-size distributions (TEM) and crystallite sizes after 100 h of milling, and differences in mean melting temperatures after the indicated milling times for mixtures with PBI

<table>
<thead>
<tr>
<th>Metal</th>
<th>metal fraction [vol.%]</th>
<th>particle diameter [μm]</th>
<th>crystallite size [nm]</th>
<th>mean $T_m$ [°C]</th>
<th>$\Delta T_{m, mean}$ 1 h</th>
<th>$\Delta T_{m, mean}$ 25 h</th>
<th>$\Delta T_{m, mean}$ 100 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>3.4</td>
<td>0.01-0.5</td>
<td>35</td>
<td>156.63</td>
<td>-1.5</td>
<td>-2.4</td>
<td>-2.1</td>
</tr>
<tr>
<td>Bi</td>
<td>2.6</td>
<td>0.02-0.5</td>
<td>50</td>
<td>271.44</td>
<td>-2.3</td>
<td>-3.7</td>
<td>-3.8</td>
</tr>
</tbody>
</table>

TEM was carried out on the edges of the mixed metal/PBI particles. Broad metal-particle-size distributions can be observed for all three mixtures (figure 5.5). However, very small particles are found for Bi and In only. Most metal particles seem to be located at the outside of the polymer particles, which is contrary to observations on thermoplastics in which metal particles are well dispersed within the polymer matrix (section 5.3). Investigation of the morphology of the particles shows some odd shapes for In. Some individual particles have a ‘splattered’ appearance as if droplets have been formed during melting after which rapid cooling has taken place. For Cu and – particularly – Bi, the shapes are more globular. Probably, the high ductility of In and – to a lesser extent – Cu is responsible for the odd shapes. The high ductility of In also becomes apparent during milling of pure In under vacuum. An In slab is formed within 1 h, whereas metal-particle agglomeration occurs much slower for Cu (cf. section 5.3). The reason that, in contrast, smaller particles are formed for In/PBI may be a stronger interaction with PBI than for Cu. More likely however, actual melting may have occurred due to the milling action, as melting point, specific heat and melting enthalpies have low values for In.

From the X-ray diffraction lines of the In/PBI mixture, the crystallite sizes are observed to decrease during milling, but are still quite large. Values are comparable to those of the Cu/PBI mixture, and somewhat narrower diffraction lines are again observed for the (111) reflections. For Bi, crystallite sizes are even larger, which is remarkable considering the low ductility of the metal. As pointed out in section 5.3, only little energy is available for deformation of the metal particles due to the presence of the hard and brittle PBI. This results in limited crystallite refinement for the metals.

DSC traces of both In/PBI and Bi/PBI (figure 5.6) show a decrease of the onset of melting of several degrees, which can already be observed after 1 h of milling. Mean values of the melting temperature of the unmilled mixture and melting-temperature depression after milling have been included in table 5.2. After milling, the melting enthalpy $\Delta H_m$ also decreases with respect to the unmilled mixture. The remaining fractions are given in table 5.3 with respect to the melting enthalpies of the unmilled mixtures. The enthalpy decrease can partly be explained by loss of metal in the vial, as in the bottom of the vial – on the tungsten carbide disc – a metal-coloured aspect is visible. However, no significant additional decrease is observed between 25 and 100 h, and the melting-enthalpy reductions scale well with the melting-temperature depressions. Therefore, it is concluded that enthalpy reduction during milling is a real effect, although the actual extent is not
Figure 5.5: TEM micrographs after 100 h of milling of (a) In/PBI, (b) Bi/PBI and (c) Cu/PBI mixtures
Figure 5.6: DSC heating traces (10 °C/min) reflecting melting endotherms after the indicated milling times for mixtures of (a) In/PBI and (b) Bi/PBI

Figure 5.7: DSC cooling traces (10 °C/min) reflecting freezing exotherms after the indicated milling times and subsequent heating for mixtures of (a) In/PBI and (b) Bi/PBI
Metal-particle sizes in metal/non-metal mixtures

<table>
<thead>
<tr>
<th>Metal</th>
<th>remaining fraction of $H_m$ after milling</th>
<th>$T_{\text{max}}$ cycling</th>
<th>remaining fraction of $H_m$ after cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 h</td>
<td>25 h</td>
<td>100 h</td>
</tr>
<tr>
<td>In</td>
<td>0.85</td>
<td>0.71</td>
<td>0.68</td>
</tr>
<tr>
<td>Bi</td>
<td>0.81</td>
<td>0.62</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Table 5.3: Remaining fraction of the melting enthalpy after milling with respect to the unmilled metal/PBI mixture, and the remaining fraction after heating to the indicated temperatures with respect to that before thermal cycling.

Undercooling is observed during controlled cooling of the melt. A decrease of the freezing temperature is observed for longer milling times (figure 5.7). Rather rough traces are observed for the unmilled mixtures, which can be ascribed to nucleation in the different larger particles that are still present in the sample. The relatively low freezing temperatures of the unmilled mixtures can be attributed to the high purity of the metals and a low amount of defects. An increase in the freezing temperature is observed for In/PBI after 1 h of milling, which can be ascribed to enhanced nucleation due to the introduction of defects or other impurity sites, while the particle size is still rather large. The reason why this effect is not seen in Bi/PBI for the same milling time is likely a difference in particle size, as Bi is much more brittle than In. Besides, Bi shows stronger undercooling than In. The freezing temperature further decreases for longer milling times, signifying a decrease of the particle size.

Undercooling is also reflected in an additional decrease of the melting enthalpy after thermal cycling, which is larger for longer milling times. Values for these additional melting-enthalpy reductions are given with respect to the (already reduced) values after milling in table 5.3. Both the undercooling effect and the decrease of the melting enthalpy are much larger for Bi than for In, but large differences between the metals have also been observed in mixtures with Al [4]. After recovery during one day at room temperature, the enthalpy returns largely to its original value. A reasonable explanation is that the melting-enthalpy reduction after thermal cycling is a result of a stronger metal-polymer interaction, which recovers after some time. A decrease of this metal-polymer interaction, which has a positive heat of mixing, explains why both melting-point depression and melting-enthalpy reduction decrease over time (days to months). Some additional enthalpy effects could be observed around 300 °C for the Bi/PBI mixture after 100 h of milling, but due to the small size and large width of the effects it was not possible to attribute these to either superheating or coagulation.

A depression of the onset of the melting temperature of 3 °C has also been observed for a mixture of In and poly(ethylene-alt-maleic anhydride) (PEMA), with the mean melting temperature shifting over −0.7 °C. Similar small changes were observed in the melting enthalpy as for the In/PBI mixture. As the effects of In/PBI and In/PEMA are comparable, it is assumed that no fundamental difference exists in the interaction between the metal and the various polymers. The particle size is therefore concluded to be responsible for the observed melting-point depression. The only additional effect of the polymer is providing some weak stabilisation of the metal particles at the surface, as...
observed by TEM. This results in a lowering of the surface energy of the metal and in melting-point depression as well as melting-enthalpy reduction, but no chemical bonds are formed.

For interactions of the metals with Al, relations have been determined with the particle size for both melting-point depression and melting-enthalpy reductions [4]. If similar interface enthalpies are assumed as in the case of Al, the values found result in particle sizes of 100 nm (In) and 86 nm (Bi) for the melting-point depressions, and 30 nm (both In and Bi) for the melting-enthalpy reductions according to equations 5.1 and 5.2, respectively. Due to loss of metal in the vial however, the ‘real’ melting-enthalpy reduction is smaller and the latter determined particle size is expectedly somewhat larger. As the heat of mixing is not known for the metal/PBI mixtures, these values are only an estimate. However, they scale quite well with the particle sizes that are observed in the TEM studies. In the metal/Al mixtures, melting-point depressions are generally larger. The broad particle-size distribution reflects the presence of many large particles, which largely determine the bulk (and thus thermal) properties of the material. This is the cause that limited melting-point depressions were observed for the metal/PBI systems. Undercoolings are larger for In and smaller for Bi with respect to the metal/Al mixtures. The significant undercoolings are an indication of dissimilar crystal structures and bonding types of the metals and the polymer, as can clearly be expected. A large similarity would lead to efficacious heterogeneous nucleation and thus to small undercoolings [12]. No clear indications were found for superheating behaviour, which implies again the absence of an orientation relation between metal particles and the polymer matrix, as is also the case for ball-milled metal-metal mixtures [4]. However, the changes during thermal cycling and the recovery effects indicate that interaction with the polymer matrix, although weak, is not negligible.

5.5 Summary and conclusions

A number of metal/non-metal systems have been investigated in order to assess the influence of the addition of a non-metallic material on the efficiency of particle size-reduction of a metal by milling. By studying particle growth and crystallite-size refinement, the various effects of milling, such as fracture, defect formation and cold welding could be investigated separately.

From milling of Ni at different temperatures, it was concluded that cold welding is suppressed at lower temperatures, while the probability of fracture remains equal. A larger effect for the suppression of cold welding however is observed in case milling takes place together with a non-metallic medium. Due to the suppression of cold welding, deformation of particles in a medium is clearly visible. However, orientation effects of crystallites can also be observed in coagulated metal particles. Coercivities and remanent magnetisations were enhanced for Ni/PBD samples, indicating the formation of single-domain particles.

Suppression of the probability of fracture is observed in some mixtures and can be attributed to the mechanical properties of the milling medium. This has been observed for Ni/PBD, various Cu mixtures, and metal/PBI mixtures. No influence on the probability of fracture was observed for milling in an organic liquid. For a liquid with a higher
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viscosity, more spacing was introduced, which resulted in smaller particles. The smallest particles and crystallites were produced during milling with a thermoplastic polymer (HDPE or PTFE). Metal particles were well embedded, and separation of the particles did not fundamentally affect the energy transfer for fracture. Milling with a highly elastic rubber (PBD), a brittle polymer (PBI) or a ceramic material (γ-Al₂O₃) had a clear effect on the crystallite size, as a large amount of energy was absorbed for either fracture of the brittle material, or transferred to the rubber as elastic energy. As a result, less energy was available for fracture of the metal.

From the melting and freezing characteristics of In/PBI and Bi/PBI mixtures, an analogy was drawn with metal/metal systems. Particle sizes determined from depression of melting temperatures and melting-enthalpy reductions were found to scale with actual particle sizes. Moreover, no specific orientation relation or chemical binding between metal and polymer could be observed. The metal particles were largely found at the surface of the polymer particles, and a weak interaction with the polymer matrix, with positive heat of mixing, was concluded from thermal cycling and recovery effects. Actual melting of In was postulated to take place during milling of the In/PBI mixture.

A largely qualitative overview has been given of various effects that may take place during milling of metals in various non-metallic environments. The significance of our conclusions lies in a better understanding and prediction of particle and crystallite refinement during mechanical milling. Additional research is expected to yield more fundamental insight in the properties of both metals and plastics. Findings on the present materials could also be used for actual applications, although more development from a technological viewpoint is needed. The materials can be useful as magnetic materials with enhanced coercivities and new metal catalysts, while expected applications of the composite materials are plating solutions, conductive plastics (polymer electrodes) and strengthened plastics.

References
