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Formation of thermodynamically unstable solid solutions in the Cu-Co system by mechanical alloying

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Cu-Co has been chosen as a model system to study phase formation during mechanical alloying in systems with components exhibiting a positive heat of mixing. Phase formation is monitored by scanning electron microscopy, x-ray diffraction, and calorimetric measurements. Although the occurrence of a single fcc Bragg pattern cannot definitely prove the alloy formation on an atomic scale, the quantitative agreement of the heat release upon decomposition of the alloy with the heat of mixing, calculated from the available thermodynamic data of the system, is regarded as clear evidence for the formation of an fcc solid solution. As a mechanism of alloy formation the dissolution of Cu and Co particles during milling is discussed. It is proposed that the formation of a homogeneous solid solution is energetically favored if the particle size is reduced below a critical value, which amounts to about 1–2 nm, depending on the composition of the alloy and the temperature. The driving force is provided by the chemical contribution of the Cu/Co interface enthalpy and by the high configurational entropy of the randomly distributed atoms in the solid solution.

I. INTRODUCTION

The formation of metastable and stable phases by mechanical alloying of elemental powder blends has been investigated in a variety of alloy systems during recent years.[1] For alloys with a negative heat of mixing, phase formation has been explained by an interdiffusion reaction of the components occurring during the milling process.[2] Metastable phase formation is only observed if the formation of stable phases is suppressed under the specific milling conditions. In particular, intermetallic compounds can be energetically destabilized due to chemical disorder introduced by the deformation during milling.[3] This often results in the formation of extended solid solutions or amorphous phases.

On the other hand, phase formation in alloy systems with positive heats of mixing is far from understood, as in these systems a diffusional reaction generally results in decomposition of the alloy. Nevertheless, the formation of solid solutions and amorphous phases upon ball milling of the elemental components has been observed in several systems with positive heats of mixing, such as Cu-Ag,[4] Cu-Cr,[5] Cu-V,[6,7] Cu-Ta,[8–10] Cu-W,[11] and Cu-Fe.[12–14]

One of the major drawbacks to understanding the mechanism of alloying in these systems originates from the lack of a quantitative description of the kinetics and the thermodynamic functions of these systems. The Cu-Co system however, which also exhibits a positive heat of mixing, has been studied extensively with respect to its decomposition behavior, from which kinetic data such as diffusion constants, interfacial free energies, and thermodynamic driving forces can be derived.[15–18] In addition, the thermodynamic functions can be determined with high accuracy by the calculation-of-phase-diagram (CALPHAD) method,[19,20] since a variety of thermodynamic measurements have been performed on the Cu-Co system. Therefore, Cu-Co has been selected as a model system to study phase formation during mechanical alloying of elemental powder blends with a positive heat of mixing.

II. THERMODYNAMIC FUNCTIONS OF THE Cu-Co SYSTEM

The thermodynamic functions of the Cu-Co system were calculated from the available thermodynamic data by utilizing the CALPHAD method.[21,22] The calculation considers the magnetic contributions as well as deviations from the regular solution model in case of the liquid and the fcc phase. However, these deviations are small so far as one can judge from the limited phase stability ranges under thermodynamic equilibrium conditions. The free energy of each phase is expressed by

$$\Delta G = x_{\mathrm{Cu}} G^0_{\mathrm{Cu}} + x_{\mathrm{Co}} G^0_{\mathrm{Co}} - TS^{\mathrm{mix}} + \Delta G^{\mathrm{ex}} , \tag{1}$$

where G^0_{Cu} and G^0_{Co} are the phase stability values derived from the recent assessment by Dinsdale,[23] x_{Cu} and x_{Co} are the atomic concentrations of Cu and Co, respectively, S^{mix} is the ideal entropy of mixing, and ΔG^{ex} is the excess free energy, given by

TABLE I. Coefficients of the thermodynamic functions for the Cu-Co system (Ref. 22).

	A_1	A_2	A_3	B_1
Liquid	39 188	2103	3754	−6.081
fcc	37 100	2895	3251	−5.194
hcp	38 141			−5.0

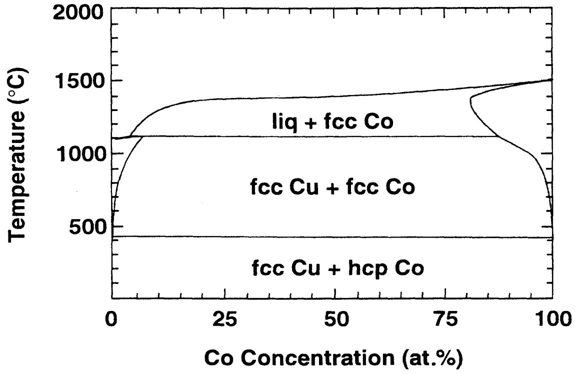

FIG. 1. Cu-Co phase diagram calculated by the CALPHAD method (Ref. 22).

$$\Delta G^{\mathrm{ex}} = A_1 x_{\mathrm{Cu}} x_{\mathrm{Co}} + A_2 x_{\mathrm{Cu}} x_{\mathrm{Co}} (x_{\mathrm{Cu}} - x_{\mathrm{Co}}) + A_3 x_{\mathrm{Cu}} x_{\mathrm{Co}} (x_{\mathrm{Cu}} - x_{\mathrm{Co}})^2 + T B_1 x_{\mathrm{Cu}} x_{\mathrm{Co}} \ . \quad (2)$$

The coefficients A_i and B_i are calculated using the thermodynamic data of the Cu-Co system and are summarized in Table I. Due to the lack of reliable solubility data for the hcp phase, the concentration dependence of its free energy can only be roughly estimated. In Fig. 1 the calculated phase diagram and in Fig. 2 the free energies of the hcp, fcc, and liquid phases are given for $T = 400\,^{\circ}\mathrm{C}$. For the Cu-Co composite during ball milling this temperature is considered as a typical interface temperature, which can, however, amount to 600 °C depending on the mechanical properties of the composite.[1,24] Figure 2 shows that the fcc phase exhibits a free energy of mixing of about 6.3 kJ/g atom for a $\mathrm{Cu_{50}Co_{50}}$ alloy at $T = 400\,^{\circ}\mathrm{C}$. As the enthalpy of mixing for the liquid phase is comparable to that of the solid solution phases, one can conclude that the positive pair exchange enthalpy originates mainly from the electronic structure of the components.

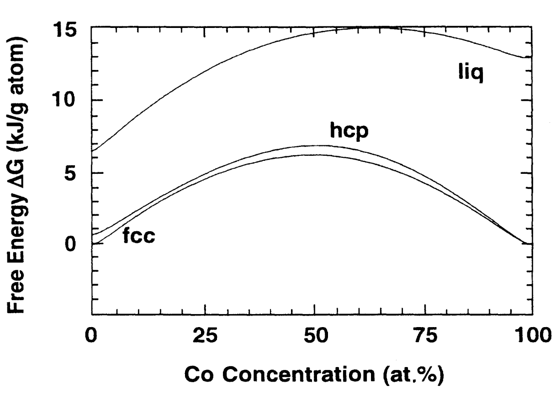

FIG. 2. Free energy ΔG of the hcp, fcc, and liquid phases at $T = 400\,^{\circ}\mathrm{C}$. The free energy of the fcc Cu and the hcp Co are taken as reference points (Ref. 22).

III. EXPERIMENTAL METHODS

As interstitial impurities might substantially influence the thermodynamics of the systems, special care has to be taken with respect to the selection of powders and the milling procedure. Therefore, all handling including the milling was carried out in glove boxes supplied with Ar via a gas purification system which maintains the oxygen and water content of the atmosphere below 1 ppm. For the alloy preparation high-purity (≤ 0.1 wt. % total metallic impurities) elemental Cu (0.6 wt. % 0) and Co (0.2 wt. % 0) powders with particle sizes between 50 and 150 μm were blended in the desired ratio to prepare alloys with Co contents between 20 and 90 at. %. The milling was performed in a planetary ball mill of type Fritsch pulverisette 5 using Cr steel vials and balls with a ball-to-powder weight ratio of 10:1. The milling was interrupted each 15 min for 15 min to cool the vials which heated up typically to about 50 °C. The milling intensity (an arbitrary rotation speed scale) was adjusted to 5 or 7 corresponding to measured rotation speeds of 153 and 228 min^{-1}, respectively. After selected milling times, small amounts of the material were taken for analysis. By energy-dispersive x-ray analysis in a scanning electron microscope the contamination with Fe due to abrasion of the milling tools was determined. For the milling intensity 5 a relatively low Fe content of 1.4 at. % was detected after 100 h of milling, whereas 43.4 at. % Fe and 6.1 at. % Cr were found after 80 h of milling with intensity 7. Therefore, only results are considered which were obtained from powders milled with intensity 5. After long mechanical alloying (100 h) an oxygen content of 0.3–0.4 wt. % was found by chemical analysis, which is comparable to the oxygen level of the initial powder blend.

As oxygen impurities have been suggested as an origin for alloy formation in systems with positive heats of mixing,[25] additional milling experiments have been performed with Cu powder, supplied by the Norddeutsche Affinerie (Germany), whose nominal oxygen content amounts to less than 0.1 wt. %.

Microstructural development during milling was observed by scanning electron microscopy on embedded, ground, and polished powders which were etched in an aqueous Cu-ammonium chloride solution. For structural characterization a Siemens D5000 Θ-Θ diffractometer equipped with a graphite secondary monochromator and a Co tube was employed. Differential scanning calorimetry (DSC) was carried out using a Perkin Elmer DSC 2 with heating rates between 2.5 and 20 K/min. Prior to the DSC experiments the system was flushed several times with 99.9999% Ar, which also was used during the experiments. As a baseline, a second run for each specimen was directly taken after the first run without changing the conditions of the measurement.

IV. RESULTS

Upon mechanical alloying an increasing particle size of the powder is observed as well as a sticking of the material to the vials and balls. This behavior is more pronounced for higher Cu concentrations and for the Cu powder with a low oxygen content. Scanning electron micrographs taken from cross sections of the powder show the typical lamellar microstructure which is often found in mechanically alloyed powders consisting of ductile components.[1] After 20 h of milling the lamella thickness of a $Cu_{50}Co_{50}$ specimen is already considerably smaller than 100 nm in some regions (Fig. 3). The microstructure is further refined with increasing milling time, and after 100 h of milling the material appears homogeneous on a submicron scale.

X-ray-diffraction (XRD) patterns from mechanically alloyed $Cu_{50}Co_{50}$ are shown in Fig. 4. After 2 h of milling only the lines of hcp Co and fcc Cu are detected. Upon further milling the peaks broaden and after 20 h of milling the integral intensities of peaks of the hcp phase decrease relative to those of the fcc phase, while the latter are shifted to higher diffraction angles, suggesting an alloying of the components. After 100 h of milling the Co peaks have fully disappeared, and the lattice parameter of the fcc phase is reduced to 0.3593 nm.

Similar results were obtained for other compositions of the powder blend and the lattice parameters of the finally formed fcc solid solutions are plotted as a function of the Co concentration in Fig. 5. The measured values are in good agreement with the data compiled by King,[26] suggesting that homogeneous fcc solid solutions are formed over the whole concentration range.

With respect to the mechanisms involved in the phase formation during mechanical alloying (see Sec. V) it is important to determine the crystallite size and the rms strain $\langle \varepsilon^2 \rangle^{1/2}$. These can be derived from the width of the diffraction peaks by utilizing the method of Williamson and Hall.[27] However, this procedure could only be applied to diffractograms taken from the early and the final stages of mechanically alloyed specimens due to overlapping of peaks for intermediate stages. The analyses show that the crystallite sizes of the solid solutions are typically in the range 30–40 nm. They are about a factor of 2 larger than those of the pure elemental components in the early stage of milling, which amount to about 15–20 nm for a powder blend of $Cu_{50}Co_{50}$. The rms strains reach values of 0.3–0.8 % for the solid solution and about 0.3% for the elemental components. These values are comparable to those observed for mechanical alloying of Cu-Fe (Ref. 14) whereas our crystallite sizes are slightly larger.

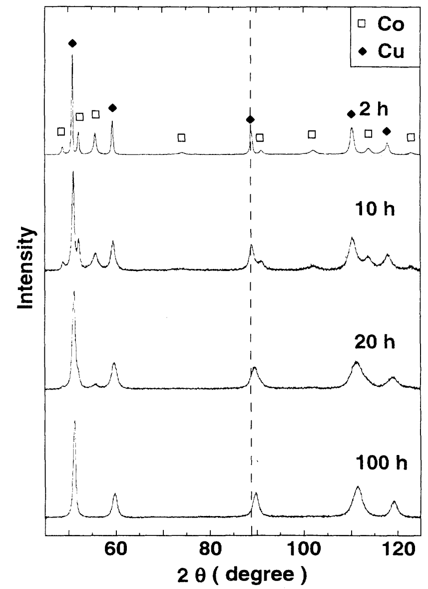

FIG. 4. XRD patterns from mechanically alloyed $Cu_{50}Co_{50}$ after selected times of milling. The characteristic diffraction peaks of the fcc Cu and the hcp Co structures are indicated.

Mechanically alloyed Cu-Co specimens with Co concentrations of 30, 50, and 70 at. % were investigated by DSC. For milling times greater than 20 h the samples exhibit a broad exothermic double peak upon heating whose intensity increases with increasing milling time (Fig. 6). This corresponds to the development of a diffraction pattern characteristic of a solid solution which has been observed for milling times longer than 20 h. For long milling times all samples exhibit a broad exothermic double peak which mainly originates from the decompo-

FIG. 3. Cross section of an etched $Cu_{50}Co_{50}$ powder blend mechanically alloyed for 20 h.

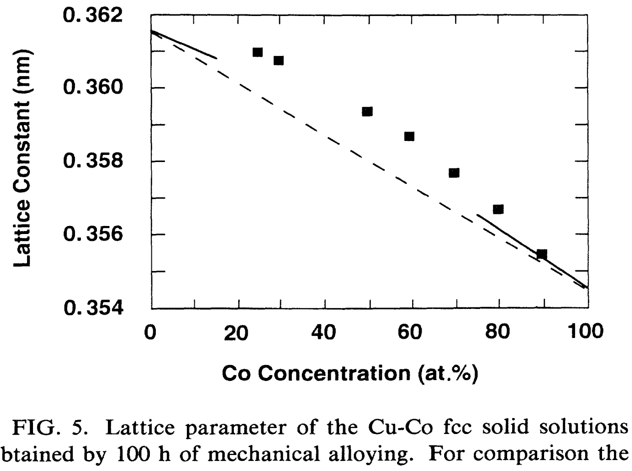

FIG. 5. Lattice parameter of the Cu-Co fcc solid solutions obtained by 100 h of mechanical alloying. For comparison the data from King (Ref. 26) are given measured for small supersaturations (solid lines) as well as the Vegard line (dashed).

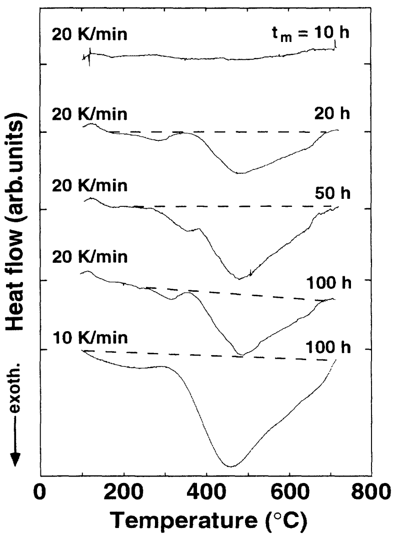

FIG. 6. DSC traces of mechanically alloyed $Cu_{50}Co_{50}$ specimen after selected times of milling taken with a heating rate of 20 K/min (10, 20, 50, and 100 h) and 10 K/min (100 h).

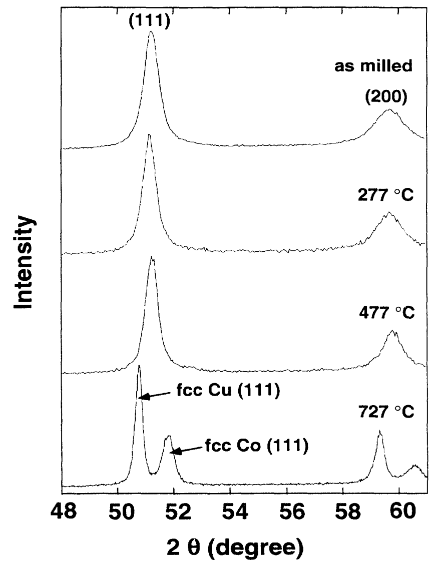

FIG. 7. XRD patterns from mechanically alloyed $Cu_{50}Co_{50}$ heated up to selected temperatures of 277, 477, and 727 °C with a rate of 10 K/min.

sition of the supersaturated fcc solid solution. Recovery may partly contribute to the heat release as observed, e.g., for mechanically alloyed Zr-Al solid solutions.[28] The DSC results indicate that for the final milling stages a heating rate of 20 K/min is too high to complete the decomposition of the Cu-Co alloys at $T=727\,°\mathrm{C}$ (the maximum temperature of our DSC). Therefore a lower heating rate was applied in these cases. Integrations of the double peak from 130 to 727 °C then yield exothermic heat releases of 8.7 12.0, and 9.8 kJ/g atom for $Cu_{30}Co_{70}$, $Cu_{50}Co_{50}$, and $Cu_{30}Co_{70}$, respectively, milled for 100 h.

In order to determine the phase reactions related to the heat release, mechanically alloyed $Cu_{50}Co_{50}$ specimens were heated up to 277, 477, and 727 °C, subsequently quenched to room temperature and analyzed by XRD (Fig. 7). Although a substantial amount of enthalpy has already been released, the specimens heated to 277 and 477 °C reveal no significant difference in the XRD patterns with respect to the as-milled solid solution.

This surprising result can be explained by the course of the decomposition reaction and the diffraction behavior of coherent phase regions. Due to the thermodynamically unstable state of the Cu-Co solid solution, it probably decomposes spinodally, whereby short-range compositional fluctuations are built up, whose concentration amplitudes are increased upon further annealing. This results in a microstructure which consists of structurally coherent areas of almost pure Cu and pure fcc Co on a very fine scale. Structural investigations on fcc Cu/Co multilayers with coherent interfaces demonstrate in agreement with the diffraction theory[29] how the x-ray patterns evolve from the bulk case if the layer thickness is decreased: Whereas the bulk pattern is observed for layer thicknesses larger than about 20 nm, one central (superlattice) reflection midway between the fcc Cu and fcc Co peaks becomes dominant with decreasing layer thickness. For layer thicknesses smaller than about 5–8 nm, a common fcc diffraction pattern is observed with an average lattice parameter.[29] Although the patterns become very similar with decreasing layer thickness to that of a homogeneous solid solution, small-angle reflections as well as satellites around the Bragg peaks prove that there is still a compositional modulation.

Considering these results, we conclude that the mechanically alloyed solid solutions decompose upon heating up to 477 °C on a scale smaller than 8 nm into almost pure Cu and Co areas. Due to the coherency of the fcc lattices the diffraction pattern appears as being from an fcc lattice with a concentration equal to the overall composition of the decomposed alloy. With respect to the initial solid solution the stored enthalpy is already substantially decreased as a result of the decomposition. Upon further heating, the Cu and Co areas coarsen and the individual bulk patterns can be observed in XRD. However, even after heating to 727 °C, some material can still be detected in the x-ray pattern which exhibits an averaged lattice constant. This indicates that the heat release determined by the DSC measurements is slightly smaller than the total enthalpy stored in the milled alloy.

It is noteworthy that the fcc Co does not transform into the hcp structure during cooling. Therefore the measured heat release should be related only to the heat of mixing of the fcc phase and not to its heat of formation. Considering the slight underestimation of the stored enthalpy by the DSC measurement, the heat releases of the mechanically alloyed phases with different Co concentrations agree reasonably well with the heat of mixing calculated by the CALPHAD method (Fig. 8). This strongly supports the assumption that homogeneous Cu-Co solid solutions are formed by mechanical alloying of elemental powder blends, despite the fact that the heat

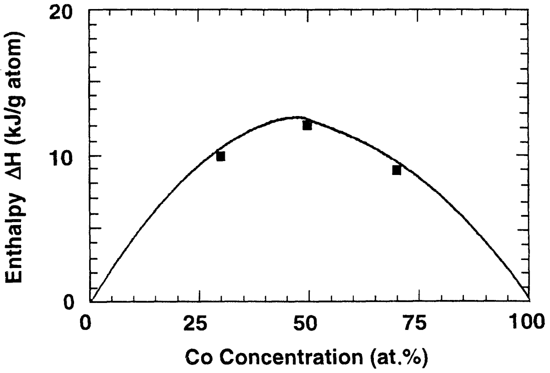

FIG. 8. Comparison of the measured heat release on decomposition of mechanically alloyed Cu-Co powder blends with the heat of mixing calculated by the CALPHAD method.

of mixing is positive. An inhomogeneous alloy, e.g., with small regions of Cu and Co, would exhibit a substantially lower heat release upon heating as the enthalpy contribution of the interfacial boundaries is much smaller than the enthalpy of mixing (see also below).

V. DISCUSSION OF THE ALLOYING MECHANISM

The mechanism by which a solid solution with a positive heat of mixing is formed upon milling is still a subject of controversy. Basically four approaches have been published to our knowledge so far. First, Veltl, Scholz and Kunze[10] suggested that the energy stored in the grain boundaries serves as a driving force for the formation of a solid solution. Their assumption was based on the observation that alloying occurs when the crystallite sizes of the elemental components decrease down to the nanometer range and that a substantial amount of enthalpy can be stored in nanocrystalline metals due to the large grain-boundary area.[30] Secondly, Yavari and Desré[25] suspected that alloying of immiscible elements originates from a high oxygen content thus resulting in a negative heat of mixing of the multicomponent mixture. Later, Yavari, Desré, and Benameur[13] proposed an alternative alloying mechanism, based on the assumption that upon deformation of the composite, fragments with small tip radii are formed such that the capillary pressure forces the atoms at the tips of the fragments to dissolve. Very recently, Eckert *et al.*[14] suggested a fourth mechanism, which explains alloy formation by an enhanced solubility due to the high dislocation density during the initial stages of milling of nanocrystalline powders.

We will show that none of these mechanisms can satisfactorily explain alloy formation in the Cu-Co system. Instead, we will emphasize the importance of the Cu/Co interfaces formed upon deformation and will show that the energetic contribution of the Cu/Co interfaces can enhance the free energy of the composite above that of the solid solution thus providing a driving force for alloying.

A. The influence of the crystallite size

Nanocrystalline metals and alloys prepared by ball milling or by inert gas condensation contain large excess enthalpies.[30,31] In particular, for high-melting metals and alloys, calorimetric measurements show that enthalpies up to 7.4 kJ/g atom are released upon recovery and recrystallization.[10,30] As the enthalpy related to internal strain is usually less than 0.1 kJ/g atom (see also below), the excess enthalpies mainly originate from the large grain-boundary area due to the small crystallite size. Therefore (averaged) grain-boundary enthalpies can be determined from the released enthalpies and the related change in crystallite size upon annealing.[31,32] During milling of elemental powder blends, the high excess enthalpies of the pure components can result in alloy formation, if the alloy has a lower free energy than the mixture of the elemental components. Indeed, alloy formation during ball milling of elemental powder blends with positive heats of mixing is, in most systems, only observed when the crystallite size of the elemental components is reduced to about 10 nm. If an amorphous phase is formed, then the grain-boundary enthalpy can provide a significant driving force for alloy formation, as observed in the Cu-Ta system by Veltl, Scholz, and Kunze.[10] However, in cases where a crystalline phase is formed, the alloy often exhibits a grain size similar to that of the elemental components. Thus no substantial gain in free energy can be expected if the grain-boundary enthalpy of the alloy is comparable to the one of the components.[13,14]

This also holds for the Cu-Co system, as the minimum crystallite size of the elemental components is relatively large, ranging from 10 to 30 nm, and the crystallite size of the solid solution is typically 30–40 nm. In order to estimate the difference in the grain-boundary free energy before and after alloying, only enthalpy contributions will be considered. An increase of the crystallite size from $d_1=10$ nm to $d_2=40$ nm corresponds to a decrease in the enthalpy of the alloy by

$$\Delta H_{\mathrm{str}}=3\sigma_{\mathrm{gb}}\bar{V}_m(1/d_1-1/d_2)=0.8\ \mathrm{kJ/g\,atom}\ , \quad (3)$$

where $\bar{V}_m$ is the average molar volume and $\sigma_{\mathrm{gb}}=0.5$ J/m^2 is the grain-boundary enthalpy of Cu as measured on nanocrystalline samples.[32] The estimated change in enthalpy of 0.8 kJ/g atom is about eight times too small to overcome the positive free energy of mixing at a $T=400\,^{\circ}\mathrm{C}$ in agreement with similar contemplations carried out for the Cu-Fe system.[13,14] Even if a large error in σ_{gb} is taken into account, this calculation demonstrates that the excess enthalpy of the nanocrystalline Cu and Co does not supply a sufficient driving force for the formation of an fcc solid solution in the Cu-Co system. Contributions from the grain-boundary energy will only become important when the grain size of the components is decreased well below 10 nm.

B. The influence of the oxygen content

Some of the alloy systems with positive heats of mixing investigated contain transition elements which exhibit a high affinity to oxygen and nitrogen. In particular for systems, e.g., Cu-Ta, Cu-V, and Cu-W, which form amorphous phases upon milling, the elemental powder components can absorb larger quantities of oxygen and nitrogen if they are not handled properly. Yavari and Desré[25] therefore assume that typically 5 at. % oxygen is dissolved in these alloys, thus decreasing their enthalpies of mixing substantially. Indeed, the reported heats of transformation from the amorphous phase to the elemental components amount to only 3–11 kJ/g atom in the case of a $Cu_{30}Ta_{70}$ alloy,[9,10] for example, which is at least a factor of 2 smaller than that expected from the thermodynamics of the Cu-Ta system.[33] The small heat of crystallization indicates the influence of impurities in these systems, which, in addition, might also determine the observed formation of the amorphous phase in favor to a solid solution. As in the Cu-Co system, the solid solution in the Cu-Ta, Cu-V, and Cu-W system has a lower free energy than the amorphous phase,[33] and should therefore be formed if impurities are avoided. Recent experiments in the Cu-V system[7] seem to support this conclusion.

In the case of the Cu-Co system, the formation of a solid solution in favor of an amorphous phase is in agreement with the thermodynamics of the system described in Sec. II. The experiments on powder blends with different amounts of oxygen show that the formation of a solid solution is also observed in alloys containing an extremely low oxygen content. Even for relatively high amounts of oxygen impurities (0.6 wt. %), DSC measurements confirm the positive heat of mixing, and no influence on its value could be determined for different oxygen concentrations, within the accuracy of the measurements. We therefore conclude that in the Cu-Co system moderate levels of oxygen impurities do not influence the phase formation and that the positive heat of mixing is not significantly decreased by impurities.

C. The influence of small tip radii

More recently, Yavari, Desré, and Benameur[13] proposed an alternative alloying mechanism for composites of Cu with Fe or other high-melting bcc metals exhibiting a positive heat of mixing with respect to Cu. The mechanism is based on the assumption that upon deformation, necking of the composite occurs and fragments with small tip radii are formed such that the capillary pressure forces the atoms of the fragments to dissolve. By assuming an enthalpy for the (incoherent) Cu/Fe interface of about 1.4 J/m^2 the model predicts a dissolution of Fe atoms in a Cu matrix for a tip diameter less than about 2–6 nm.

A similar mechanism has also been considered in filamentary microcomposites consisting of discontinuous filaments with diameters in the submicron range. However, in these composites the filaments spheroidize as soon as atomic mobility is possible.[34,35] This behavior is in good agreement with theoretical predictions[36,37] which consider the interaction of the solute atom with regions of the filament exhibiting a larger curvature than the tip radius. One would therefore expect that also during mechanical alloying the elongated particles do not dissolve but rather spheroidize, if small tip radii and necking of the filaments occur.

D. The influence of the enhanced dislocation density

A high dislocation density may contribute significantly to the atomic level strain as observed in nanocrystalline metals and alloys prepared by ball milling.[30] As mentioned above, the energetic contribution is however small, and therefore, cannot serve as a driving force for alloy formation. Nevertheless, a high dislocation density might cause a substantial increase in the mutual solubility due to the change in the chemical potential of the solute atom in the strain field of the dislocation which has been suggested as an alloying mechanism in the Cu-Fe system.[14] The enhanced solubility can originate from the parelastic interaction between the strain field of an edge dislocation and a solute atom, if the atomic size difference of the alloy components determines the positive heat of mixing. For example, such a behavior is expected in the Cu-Ag system where the atomic size difference of the components determines mainly the terminal solubilities. However, this enhanced solubility is metastable as the driving force for the decomposition is also increased in the strain field of the dislocation.[38] Within the linear elasticity theory this results in the same solubilities as observed under equilibrium conditions, e.g., the equilibrium phase diagram is still valid in the vicinity of the dislocation. It is therefore questionable, whether the metastable enhancement of the solubility in the strain field of a dislocation can yield a dissolution of Cu and Co regions.

In addition, it should be noted that the positive heats of mixing in systems such as Cu-Co and Cu-Fe do not originate from the atomic size mismatch of the atoms (see also Sec. II). Instead, the positive pair exchange enthalpy is mainly caused by the electronic structure of the components which does not allow for a decrease of the total electronic enthalpy upon alloying. In order to explain the formation of a solid solution during ball milling the mechanism proposed by Eckert *et al.*,[14] i.e., changes of the electronic structure in the strain field and in the core of the dislocation, have to be considered.

On the other hand, transmission electron microscope investigations on supersaturated Cu(Co) alloys do not indicate any preferred precipitation of Co particles in the strain field of the dislocation or in the vicinity of a grain boundary.[18] This, however, would be expected if the solubility is enhanced in these regions.[38] Therefore, the assumption of an enhanced solubility due to the high dislocation density as a mechanism of phase formation during mechanical alloying seems unlikely in the Cu-Co system.

E. The influence of coherent Cu/Co interfaces

In addition to the decrease of the crystallite size in the elemental components upon milling, which gives rise to an excess enthalpy as described in Sec. V A, Cu/Co interfaces are formed. Besides the structural excess enthalpy, these interfaces also exhibit an excess chemical enthalpy originating from the unlike neighbors across the interface. This chemical contribution σ_{chem} can be calculated from the thermodynamics of the system by applying Becker's model[39] if the alloy behaves like a regular solution. As shown by the CALPHAD calculations (Sec. II), this is reasonably fulfilled in the case of the fcc Cu-Co alloy. The pair exchange enthalpy required in Becker's model can most favorably be derived from the CALPHAD calculation.[40] With the coefficients in Table I, the chemical contribution to the interface enthalpy amounts to about 0.2–0.3 J/m^2, depending on the crystallographic orientation of the crystallites. This value has been recently confirmed by investigations on the precipitation kinetics of supersaturated Cu-Co alloys.[18]

The difference in the excess chemical enthalpy between the composite and the alloy formed depends only on the size of the elemental regions of the composite, since the interface enthalpy in the (homogeneous) alloy contains no chemical contribution. The sizes of the elemental components have been estimated by their crystallite sizes as derived from the analysis of the x-ray-diffraction pattern.[13,14] By using Eq. (3) this results in a chemical contribution of the interface enthalpy which amounts to less than 1 kJ/g atom for Cu-Co and Cu-Fe composites with a crystallite size of 10 nm. Yavari, Desré, and Benameur,[13] and Eckert *et al.*[14] therefore rule out that the chemical contribution of the interface enthalpy can serve as a driving force for alloy formation.

However, the crystallite size as determined by analysis of the XRD pattern may not be a good approximation for the size of the elemental components during milling, as the formation of coherent interfaces between Cu and Co regions does not change the crystallite size. This is, in particular, demonstrated by investigations on Cu/Co multilayers which exhibit coherent interfaces and crystallite sizes much larger than their layer thicknesses.[29] Therefore, the thickness of the elemental components in the final state may be much smaller than their crystallite sizes thus enhancing the chemical enthalpy contribution of the interface.

This conclusion is also supported by the x-ray investigations. The disappearance of the two distinct diffraction patterns from Cu and Co upon milling and the simultaneous development of a pattern from a superlattice is only possible if the Cu and Co regions become coherent and their sizes are reduced below 5–8 nm. In the case of the Cu-Fe system, only for Cu and Fe particles smaller than about 5 nm (Ref. 41) do the distinct fcc and bcc diffraction patterns disappear. This, however, has been observed on mechanical alloying of $Cu_{50}Fe_{50}$ powder blends.[12–14] We therefore conclude that the Cu and Co regions develop a deformation texture and become coherent, while they are reduced upon milling well below 10 nm. This requires a transformation of the hcp Co into the fcc structure which, however, is reasonable in view of the small difference in free energy between the hcp and the fcc structure and the lower interface enthalpy of a coherent interface. The mechanism of further refinement of the microstructure is possibly determined by dislocation motion leading to a shearing and cutting of particles.

The refinement of the microstructure enhances the chemical contribution of the interface enthalpy as shown in Fig. 9 for different sizes of the Cu and Co regions. Taking into account an enthalpy of 0.3 J/m^2 for a coherent Cu/Co interface, a reduction of the Cu and Co particle sizes down to about 1 nm raises the enthalpy of a $Cu_{50}Co_{50}$ composite above 6 kJ/g atom, which is sufficient to allow for a phase transformation of the composite into a solid solution, in particular for temperatures $T > 400\,°C$. In this case the solid solution is of lower free energy than the elemental components. The critical sizes d_c below which the chemical contribution of the Cu/Co interface enthalpy exceeds the free energy of the solid solution can be calculated from a simple energy balance. Again, the (small) entropy contribution to the free energy of the interface is neglected. Thus

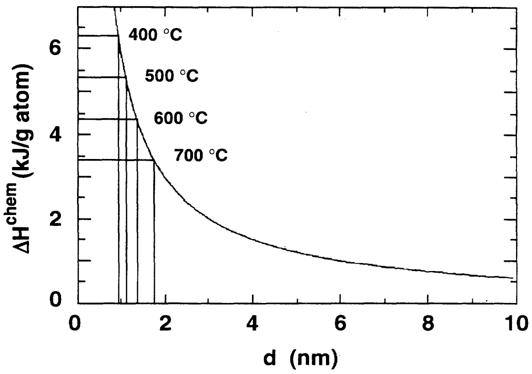

FIG. 9. The chemical contribution ΔH_{chem} of the Cu/Co interfaces to the enthalpy of a $Cu_{50}Co_{50}$ composite as a function of the size d of the Cu and Co regions, calculated for an interface enthalpy of 0.3 J/m^2. In addition, critical sizes d_c are indicated for different temperatures following Eq. (4).

$$\frac{3\sigma_{chem}\bar{V}_m}{d_c} = H_{mix} - TS_{mix}$$

and (4)

$$d_c = \frac{3\sigma_{chem}\bar{V}_m}{H_{mix} - TS_{mix}} .$$

In these equations H_{mix} and S_{mix} are the heat of mixing and the entropy of mixing, respectively.

The formation of the solid solution can be viewed as an order-disorder transition, whereby the enthalpy is increased. The driving force originates mainly from the entropy of mixing of the disordered alloy which is much larger than the entropy of the phase-separated composite. Thus the local temperature at the interface during milling is important for the formation of a solid solution. This can be seen from Fig. 9 where the critical sizes d_c of the Cu and Co regions are indicated for different temperatures. Accordingly, the Cu and Co particles have to be reduced to 1–2 nm in order to allow a phase transformation for temperatures ranging from 400 to 700 °C.

The critical particle sizes calculated above are only lower limits as a decrease of the (structural) enthalpy due to recrystallization during alloy formation (see Sec. V A), and the reduction of the atomic strain results in an in-

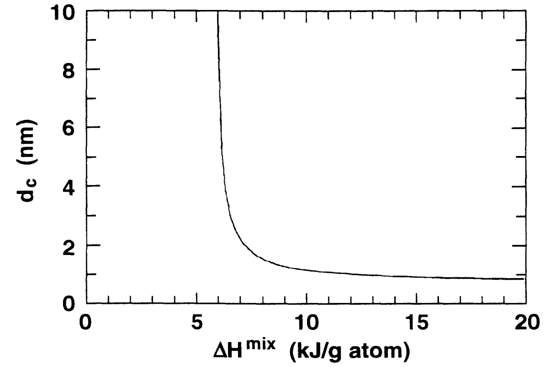

FIG. 10. The critical size d_c of elemental regions in a composite as a function of the enthalpy of mixing $H_{\rm mix}$ of the alloy formed.

crease of d_c. The enthalpy related to the strain can be estimated by

$$\Delta H_{\rm el}=\tfrac{1}{2}E\varepsilon^2\bar{V}_{\rm mol} , \tag{5}$$

where E is the Young's modulus of elasticity and ε is the strain. Using $E=130$ GPa for copper, $\Delta H_{\rm el}$ amounts to only 46 J/g atom for $\varepsilon=1\%$. Therefore, the influence of the elastic strain on d_c can be neglected in the Cu-Co system but might be important in systems exhibiting large size differences in atomic radii.

As Eqs. (4) show, the critical particle size also depends on the heat of mixing. By assuming that the molar volume, the magnetic contribution to the free energy of mixing and the entropy of mixing are independent of the enthalpy of mixing, an increase of $H_{\rm mix}$ up to 20 kJ/g atom decreases d_c down to 0.78 nm at $T=400\,^{\circ}{\rm C}$ (Fig. 10), whereas $H_{\rm mix}=7$ kJ/g atom results in $d_c=2.8$ nm (for $H_{\rm mix}=6$ kJ/g atom, d_c diverges because $G_{\rm mix}=0$). This indicates that the formation of a solid solution upon ball milling is more difficult in systems with large positive heats of mixing, despite the fact that the interface enthalpies also increase with $H_{\rm mix}$.

Finally, it is interesting to note that for magnetic systems the magnetic ordering is usually decreased when the composite transforms into the solid solution. This is energetically unfavorable and results in a smaller d_c in the case of magnetic systems, for a given (chemical) heat of mixing. Therefore, magnetic systems with a large positive heat of mixing most likely do not form solid solutions, in particular, if the crystal structure of the components exhibits a high thermodynamic stability with respect to a common structure for both components which impedes the formation of coherent interfaces. This result is supported by recent investigations on the Ag-Fe system, where even after extended milling of $\rm Ag_{50}Fe_{50}$ only small mutual solid solutions in Fe and Ag are observed.[42]

VI. SUMMARY AND CONCLUSIONS

Phase formation during mechanical alloying of Cu-Co elemental powder blends has been characterized by x-ray investigations and DSC analyses. The occurrence of a single fcc Bragg pattern cannot be taken as definite evidence for a solid solution on an atomic scale. This has been demonstrated by x-ray investigations on Cu/Co multilayers[29] and on decomposed Cu-Co solid solutions. Although these materials consist of separate fcc Cu and fcc Co regions they exhibit a diffraction pattern which can hardly be distinguished from the XRD pattern of a solid solution having the same overall composition, if the Cu and Co regions are coherent and their size is smaller than about 5–8 nm. Therefore Bragg peaks of an fcc phase cannot be used as proof for the formation of a homogeneous solid solution during ball milling.

On the other hand, DSC measurements are extremely sensitive to alloy formation, as the thermodynamics of a system are mainly determined by the nearest-neighbor environment of the atoms. Thus the agreement of the heat release upon decomposition of mechanically alloyed Cu-Co elemental powder blends with the heat of mixing calculated by the CALPHAD method is clear evidence for the formation of a solid solution.

This can also be elucidated by the following consideration: If the mechanically alloyed specimen still consisted of separate fcc Cu and fcc Co regions, they would have to have a size smaller than 0.5 nm in order to release an enthalpy of 12 kJ/g atom upon coarsening [see Eq. (3) with $\sigma_{\rm chem}=0.3$ J/m^2]. This, however, is unreasonable from a structural point of view as the lattice constants amount to >0.35 nm (Fig. 5). In addition, a composite with Cu and Co regions of 0.5-nm size would have a higher free energy than the solid solution, as for example shown in Fig. 9, and would therefore also be thermodynamically unstable. Therefore, we can definitely conclude from our DSC measurements that in the Cu-Co system an fcc solid solution is formed upon mechanical alloying of elemental powder blends despite their positive heat of mixing.

The formation of the solid solution in the Cu-Co system cannot be explained by the mechanisms proposed in the literature. Instead the chemical contribution of the (coherent) interface enthalpy is believed to serve as the main driving force for alloy formation. As the free energy of mixing amounts to about 6.3 kJ/g atom for a $\rm Cu_{50}Co_{50}$ solid solution at $T=400\,^{\circ}{\rm C}$, the Cu and the Co regions of the composite have to be reduced down to 1–2 nm during ball milling in order that the interface enthalpy exceeds the free energy of mixing.

In the final state the refinement of the microstructure is believed to occur by dislocation movement leading to a shearing of coherent Cu/Co regions. The mechanism of alloy formation may therefore be comparable to the dissolution of precipitates in the persistent slip bands during cyclic deformation as observed in aged Cu-2 at. % Co alloys.[43,44] An enhanced solubility in the strain field of the dislocation can favor this process,[45] but the main driving force for alloy formation remains the interface free energy. The critical size below which the heterogeneous composite becomes unstable is therefore comparable to the critical size of nucleation in supersaturated alloys or, for spinodally decomposing alloys, to the critical wavelength below which concentration fluctuations decay during annealing. Consequently, the critical size of the microstructure depends on the temperature, the overall composition and the thermodynamics of the system.

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[1] C. C. Koch, *Mechanical Milling and Alloying,* in Materials Science and Technology, Vol. 15, edited by R. W. Cahn, P. Haasen, and E. J. Kramer (VCH, Weinheim, 1991), p. 193.

[2] R. B. Schwarz, R. R. Petrich, and C. K. Saw, J. Non-Cryst. Solids **76**, 281 (1985).

[3] M. Oehring, Z. H. Yan, T. Klassen, and R. Bormann, Phys. Status Solidi A **131**, 671 (1992).

[4] K. Uenishi, K. F. Kobayashi, K. N. Ishihara, and P. H. Shingu, Mater. Sci. Eng. A **134**, 1342 (1991).

[5] Y. Ogino, T. Yamasaki, S. Murayama, and R. Sakai, J. Non-Cryst. Solids **117/118**, 737 (1990).

[6] T. Fukunaga, M. Mori, K. Inou, and U. Mizutani, Mater. Sci. Eng. A **134**, 863 (1991).

[7] K. Sakurai, M. Mori, and U. Mizutani, Phys. Rev. B **46**, 5711 (1992).

[8] T. Fukunaga, K. Nakamura, K. Suzuki, and U. Mizutani, J. Non-Cryst. Solids **117/118**, 700 (1990).

[9] K. Sakurai, Y. Yamada, C. H. Lee, T. Fukunaga, and U. Mizutani, Mater. Sci. Eng. A **134**, 1414 (1991); Appl. Phys. Lett. **57**, 2660 (1990).

[10] G. Veltl, B. Scholz, and H.-D. Kunze, Mater. Sci. Eng. A **134**, 1410 (1991).

[11] E. Gaffet, C. Louison, M. Harmelin, and F. Foudot, Mater. Sci. Eng. A **134**, 1380 (1991).

[12] K. Uenishi, K. F. Kobayashi, S. Nasu, H. Hatano, K. N. Ishihara, and P. H. Shingu, Z. Metallkd. **83**, 132 (1992).

[13] A. R. Yavari, P. J. Desré, and R. Benameur, Phys. Rev. Lett. **68**, 2235 (1992).

[14] J. Eckert, J. C. Holzer, C. E. Krill, III, and W. L. Johnson, J. Appl. Phys. **73**, 2794 (1993).

[15] I. S. Servi and D. Turnbull, Acta Metall. **14**, 161 (1966).

[16] H. Wendt and P. Haasen, Scr. Metall. **19**, 1053 (1985).

[17] F. K. LeGoues and H. I. Aaronson, Acta Metall. **32**, 1855 (1984).

[18] R. Hattenhauer, Ph.D. thesis, University of Göttingen, 1992 (unpublished).

[19] H. L. Lukas, J. Weiss, and E.-T. Henig, CALPHAD **6**, 229 (1982).

[20] R. Bormann and K. Zöltzer, Phys. Status Solidi A **131**, 691 (1992).

[21] M. Hasebe and T. Nishizawa, CALPHAD **4**, 83 (1980).

[22] R. Bormann and R. Busch (unpublished).

[23] A. T. Dinsdale, CALPHAD (to be published).

[24] A. K. Bhattacharya and E. Arzt, Scr. Metall. (to be published).

[25] A. R. Yavari and P. J. Desré, Mater. Sci. Forum **88-90**, 43 (1992).

[26] H. W. King, J. Mater. Sci. **1**, 79 (1966).

[27] G. K. Williamson and W. H. Hall, Acta Metall. **1**, 22 (1953).

[28] E. Ma and M. Atzmon, Phys. Rev. Lett. **67**, 1126 (1991).

[29] C. Michaelsen *et al.* (unpublished).

[30] H. J. Fecht, E. Hellstern, Z. Fu, and W. L. Johnson, Metall. Trans. **21A**, 2333 (1990).

[31] A. Tschöpe, R. Birringer, and H. Gleiter, J. Appl. Phys. **71**, 5391 (1992).

[32] B. Günther, A. Kumpmann, and H.-D. Kunze, Scripta Metall. **27**, 833 (1992).

[33] R. Bormann (unpublished).

[34] R. Bormann, J. Appl. Phys. **54**, 1479 (1983).

[35] S. Hansknecht, Ph.D. thesis, University of Göttingen, 1982.

[36] H. E. Cline, Acta Metall. **19**, 481 (1971).

[37] J. van Suchtelen, J. Crystallogr. Growth **43**, 28 (1979).

[38] S. Q. Xiao and P. Haasen, Scr. Metall. **23**, 365 (1989).

[39] R. Becker, Ann. Phys. **32**, 128 (1938).

[40] R. Bormann and C. Borchers, DPG Verhandlg. **8**, 1274 (1991).

[41] C. Gente, M. Oehring, and R. Bormann (unpublished).

[42] J. Kuyama, H. Inui, S. Imaoka, S. Nasu, K. N. Ishihara, and P. H. Shingu, Jpn. J. Appl. Phys. **30**, L854 (1991).

[43] H. Mughrabi, *4th Risø International Symposium on Metallurgy and Materials Science,* edited by J. B. Bilde-Sørensen, N. Hansen, A. Horsewell, T. Leffers, and H. Lilholt (Risø National Laboratory, Roskilde, Denmark, 1983), p. 65.

[44] K. Differt, U. Essmann, and H. Mughrabi, Phys. Status Solidi A **104**, 95 (1987).

[45] H. Gleiter, Acta Metall. **16**, 455 (1968).

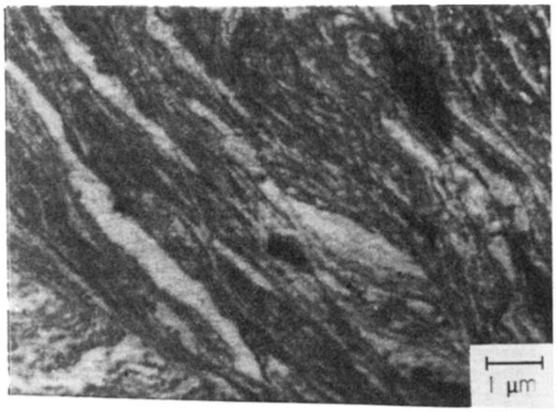

FIG. 3. Cross section of an etched $Cu_{50}Co_{50}$ powder blend mechanically alloyed for 20 h.