Structural Changes during High-Energy Ball Milling of Iron-Based Amorphous Alloys: Is High-Energy Ball Milling Equivalent to a Thermal Process?

M. L. Trudeau and R. Schulz
Vice-Présidence Recherche, Institut de Recherche d'Hydro-Québec,
1800 Montée Ste-Julie, Varennes, Québec, Canada J0L 2P0

D. Dussault and A. Van Neste
Département de Mines et Métallurgie, Université Laval, Québec, Québec, Canada G1K 7P4

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We report the first study of the effect of high-energy mechanical deformation on amorphous iron-based metallic alloys. The structural changes happening in amorphous iron-based materials containing Co or Ni during mechanical deformation show that the structural stabilities of an amorphous alloy against a thermal and against a mechanical process are not related. Therefore, the concept of a high local effective temperature during the milling process cannot be singled out as the only reason for the observed structural transformations.

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The discussion over the structural changes observed in alloys during high-energy mechanical deformation, as well as the underlying mechanism for the reaction and, in particular, the effective temperature present in the metallic powder during the milling process, is still surrounded by controversy.[1-7] The production of a large number of structural defects which drives the structure into the amorphous state[3] or the presence of a high "local effective temperature" at the collision site which gives rise to a solid-state-type reaction process[2] are examples of mechanisms that have been proposed to explain the amorphization reaction which takes place during the high-energy mechanical alloying of some pure elemental powders or intermetallic compounds. Eckert *et al.* proposed that this local effective temperature is proportional to the milling intensity in order to explain the limited mechanical energy range associated with the amorphization process.[2]

To get a better understanding of the mechanisms responsible for the structural changes occurring during high-energy mechanical deformation we have opened a new route of investigation: we study the structural transformations of already amorphous transition-metal–metalloid materials when submitted to high-energy deformation, with and without the incorporation of some crystalline elements.

Two amorphous ribbons were obtained from Allied Metglas Products: Metglas 2605CO ($Fe_{66}Co_{18}Si_1B_{15}$) and Metglas 2605S-2 ($Fe_{78}Si_9B_{13}$). Around 5.0 g of ribbon were cut into pieces and put in an argon-atmosphere cylindrical steel container (70-ml maximum load) with two $\frac{7}{16}$-in.- and one $\frac{9}{16}$-in.-diam steel balls. The mechanical deformation was performed with SPEX 8000 laboratory ball mill. For some experiments, Ni (99.9% pure) or Co (99.8% pure) powders were incorporated at the beginning of the process. The structure of the mixture was studied throughout the deformation using a Philips x-ray diffractometer equipped with Mo $K\alpha$ radiation. The amorphous state was also investigated with a Perkin-Elmer DSC-4 differential scanning calorimeter.

Surprising results can be seen in Fig. 1 which shows the effects of the high-energy milling on the structure of Metglas 2605CO. The amorphous powder becomes completely crystalline after about 24 h of mechanical deformation. The first crystalline phase, α-Fe(Co), is visible in the x-ray pattern after 3 h of milling while the second boride phase, $[Fe(Co)]_2B$, appears after 12 h. The DSC scans in Fig. 2 also show the important changes occurring in the microstructure of the alloy. The first exothermic peak at around 441 °C (maximum heat flow) is associated with the precipitation of α-

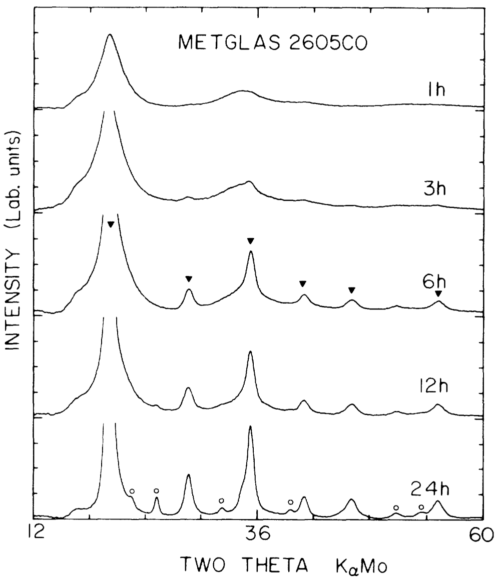

FIG. 1. X-ray spectra of Metglas 2605CO powders as a function of milling time. (▼) α-Fe(Co); (○) $[Fe(Co)]_2B$.

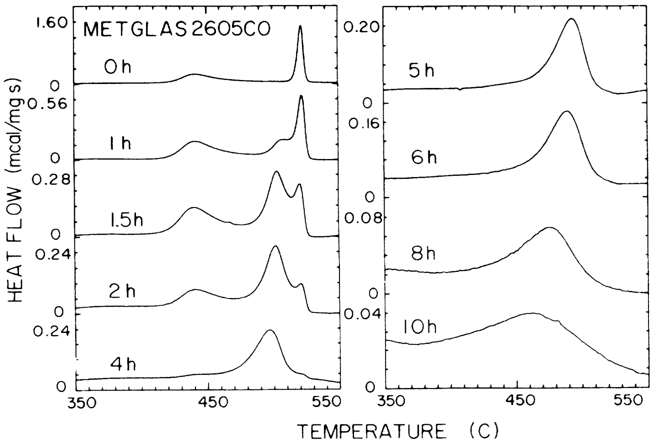

FIG. 2. Differential scanning galorimetry of Metglas 2605CO powders as a function of milling time at a rate of 20 °C/min.

Fe(Co).[8] Its intensity decreases with increasing milling time, vanishes after about 4 h, and is inversely proportional to the intensity of the α-Fe(Co) x-ray peaks. The second DSC peak at around 521 °C is associated with the crystallization of the boride phase. This peak splits into a double peak with increasing milling time. The one at 521 °C decreases in intensity and vanishes after about 4 h while a second peak located at a slightly lower temperature grows from the beginning of the process, reaches a maximum intensity around 4 h, and decreases afterward. Its position shifts to lower temperature values with increasing milling time and the peak becomes wider. Detailed x-ray analysis shows that this peak also corresponds to the crystallization of the same boride phase and therefore some microstructural or chemical changes must occur during the first few hours of milling which alter the nature of the crystallization process. Previous works[9,10] have shown that the crystallization temperature of amorphous materials obtained through mechanical alloying can be very dependent upon the presence of impurities and in particular oxygen. In our case, even though all our experiments have been done in an argon-atmosphere glove box, oxygen has increased from 0.05 wt.% in the amorphous ribbons to about 0.60 wt.% in all the powders after 24 h of milling.

Figure 3 shows the same measurements made on Metglas 2605S-2 before and after 24 h of milling. After this period of time, only one crystalline phase, α-Fe(Si), is visible in the x-ray pattern. The first DSC peak has disappeared and, like in the previous case, the second DSC peak has shifted from 575 °C for the amorphous ribbon to 505 °C for the final powder. For both alloys the activation energy for the thermal crystallization of α-Fe(Co,Si) does not change during the milling process while the activation energy for the thermal crystallization of the boride phase decreases as the peak shifts to lower temperatures. According to these results, the less thermally stable alloy, the Metglas 2605CO (T_{x1} $=441$ °C), crystallizes much more rapidly during ball milling than the cobalt-free alloy ($T_{x1}=553$ °C). This could be in agreement with the existence of a local effective temperature of the order of the crystallization temperature of the Metglas 2605CO.

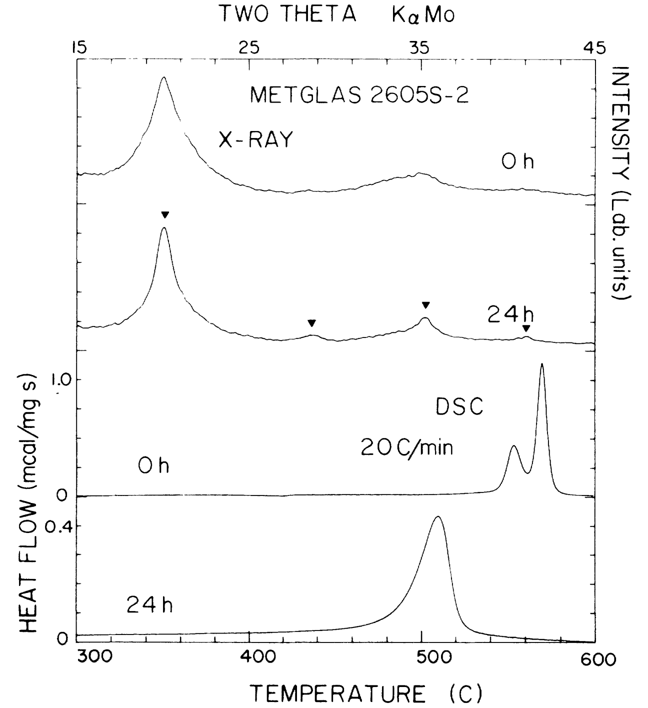

FIG. 3. X-ray and DSC data of Metglas 2605S-2 for the as-quenched amorphous ribbons and the powders after 0 and 24 h of high-energy mechanical deformation. (▼) α-Fe(Si).

In order to investigate the compositional dependence of this process some amounts of Co and Ni were incorporated in the more stable alloy, the Metglas 2605S-2. The results of adding 8 at.% of Co (final composition $Fe_{72}Co_8Si_8B_{12}$) and 17 at.% of Ni ($Fe_{65}Ni_{17}Si_7B_{11}$) are presented in Figs. 4 and 5. In the first case, the Co diffuses rapidly in the amorphous alloy during the early stage of the milling process and induces a rapid and complete crystallization of the amorphous powder. In the Ni case, the Ni diffraction lines disappear almost completely during the first 4 h and a complete amorphous powder is obtained after 12 h of milling. More interesting is the fact that the powder continues to stay amorphous after more milling. Figure 6 shows the important changes observed in the DSC traces of these powders taken throughout this amorphization process. The two high-temperature peaks of the nickel-free amorphous matrix located at 553 °C and 570 °C have been replaced after 24 h of milling by two low-temperature peaks located at around 375 °C and 480 °C, the first DSC peak still being the crystallization of the α-Fe phase. The crystallization temperature of this powder is lower than the crystallization temperatures of the Metglas 2605CO. The amorphous powder containing the Ni

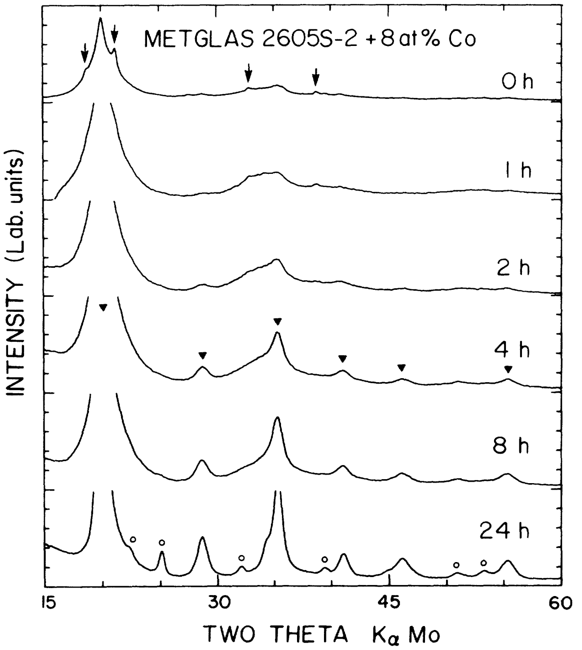

FIG. 4. X-ray traces showing the effects of adding 8 at.% of Co to Metglas 2605S-2; the powder is completely crystalline after 24 h of milling. (↓) Co peaks; (▼) α-Fe(Co); (o) [Fe(Co)]$_2$B.

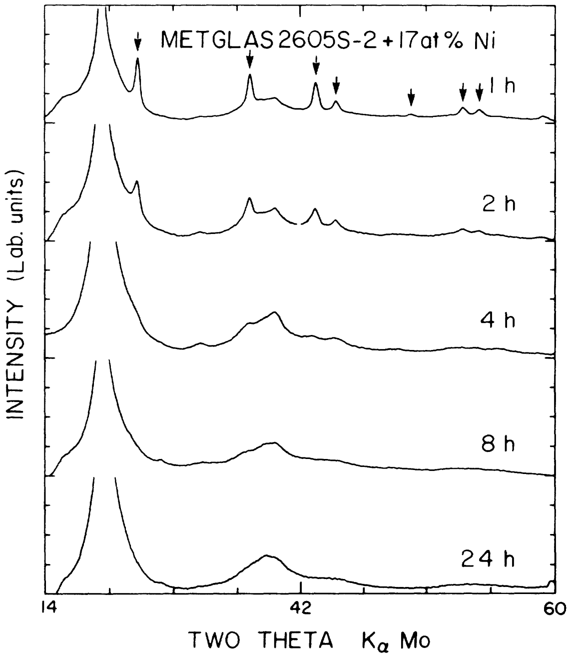

FIG. 5. X-ray traces showing the effect of adding 17 at.% of Ni to Metglas 2605S-2; the powder is completely amorphous after 24 h of milling. (↓) Ni peaks.

is therefore less thermally stable than the Metglas 2605CO but more stable against mechanical crystallization. Moreover, the activation energies for the thermal crystallization of this powder are 1.8 and 2.4 eV, respectively, compared with 4.0 and 3.5 eV for the Metglas 2605S-2 alloy, and 2.2 and 3.5 eV for the 2605CO case. These experiments show clearly that the ratio between the local effective temperature at the collision site and the crystallization temperature of an amorphous alloy is not the only criterion to explain the relative stability of an amorphous structure against high-energy mechanical deformation.

The structural stability of the amorphous Metglas 2605S-2 plus Ni powder against mechanical deformation together with the low crystallization temperature of the alloy and the small activation energy for thermal crystallization suggests that the effective temperature in the powder between the colliding steel balls is much lower than what was suggested before. These results are more in agreement with our recent study of the interdiffusion process during mechanical alloying of Ni-Zr where an effective temperature of about 280 °C was estimated.[6]

At the present stage, it seems that often more than one mechanism is needed to explain the structural transformations that are happening during high-energy mechanical deformation. The differences in behavior between the Co and the Ni addition are quite dramatic and suggest that the apparition of crystallites in our experiments seems to be related more to the alloy chemical composition than to its crystallization temperature. In fact, a possible explanation for this difference in behavior can be found in the phase diagrams of Fe-Ni and Fe-Co.[11] Co forms a solid solution with Fe while the solubility limit of Ni in α-Fe at 300 °C is about 8 at.%. Therefore, in the amorphous alloy containing 17 at.% of Ni, chemical segregation of the Ni atoms is required in order to precipitate the α-Fe crytalline phase. In other words, some amount of Ni will have to be expelled from the α-Fe nuclei in order for the crystallization to take place. Therefore, the addition of Ni to the Metglas alloy stabilizes the amorphous structure against mechanical cry-

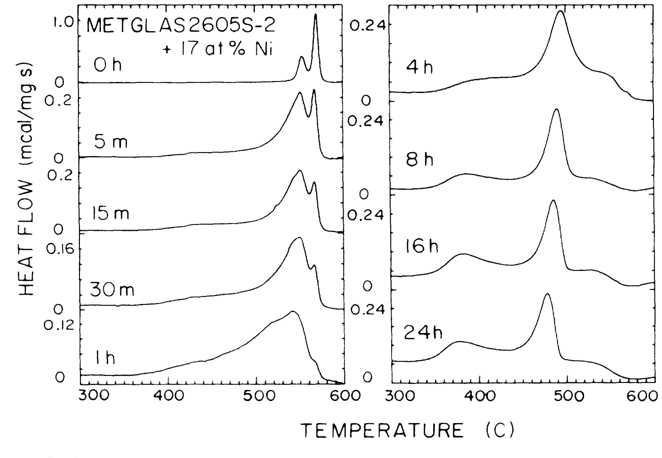

FIG. 6. DSC traces of Metglas 2605S-2 with 17 at.% of Ni as a function of milling time at a rate of 20 °C/min.

stallization. Preliminary results on the addition of a smaller amount of Ni (Ref. 12) show that the minimum concentration of Ni required in order to obtain a mechanically stable amorphous phase is indeed around 8 at.% in agreement with the phase diagram. For the amorphous alloy containing Co, nothing can impede the crystallization of the α-Fe since Co is totally miscible in this crystalline phase up to a concentration of about 75 at.%. In fact, the mechanical precipitation of the α-Fe(Co) is accelerated by the addition of Co to the amorphous phase probably because of a reduction in the effective nucleation barrier. Since the heat of mixing between Fe and Co is not very large, this reduction in the nucleation barrier is probably associated with a change in the surface energy between the nucleus and the amorphous matrix.

These experiments have shown that the crystallization due to a thermal process and the one induced by high-energy mechanical deformation can be very different. The direct relation between these two processes that is often made should then be done with great caution. This study also reveals the important role that one chemical element may play in the structural transformation occurring during high-energy mechanical deformation. The addition of Co to a mechanically fairly stable amorphous material induces its rapid crystallization while the addition of Ni gives rise to a perfect mechanically stable amorphous material. This Ni-based alloy is, however, much less thermally stable than the corresponding Ni-free amorphous alloy since its crystallization temperature, as well as its activation energy for thermal crystallization, is much lower. The effect of Ni or any other nonmiscible element in α-Fe could then be used to facilitate the amorphization process or to stabilize an amorphous iron-based material against high-energy mechanical deformation.

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