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Metastable melting phenomena and solid state amorphization (SSA) by mechanical alloying

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1. Introduction

The melting temperature of a metastable phase of a material is always lower than that of the stable phase. When a substance with a metastable crystalline structure is heated continuously, the liquid phase is produced at the melting temperature of the metastable crystalline phase. However, at this melting temperature, the liquid phase is also metastable relative to the stable crystalline phase. On further heating, crystallization of the liquid phase may take place to form the stable crystalline phase. Heating to a higher temperature results in the re-emergence of the liquid phase when the melting temperature of the stable phase is reached.

Such repeated melting during the course of a continuous rise in temperature may be observed as a stable phase equilibrium for an alloy with a retrograde solidus line. However, by forming metastable phases, using rapid solidification or vapour quenching [1], numerous cases of repeated melting on heating can be observed.

Recently, in many alloy systems, the formation of amorphous phases has been reported using the mechanical alloying technique. Since the free energy of the amorphous phase is close to that of the supercooled liquid, the amorphization by mechanical alloying may also be explained in terms of metastable melting. The purpose of this study is to investigate several metastable melting phenomena, in pure metals and alloys, in order to explain thermodynamically solid state amorphization by the mechanical alloying process.

2. Metastable melting of pure substances

Figure 1 shows a schematic diagram of the Gibbs' free energies of various phases of a pure substance. In Fig. 1, when the metastable solid γ is formed, by raising the temperature of solid γ to T_m^γ it should melt to form the liquid phase. When T_m^γ is sufficiently low to give a liquid viscosity of around 10^{12} P, such melting may be called "solid state amorphization" [2, 3].

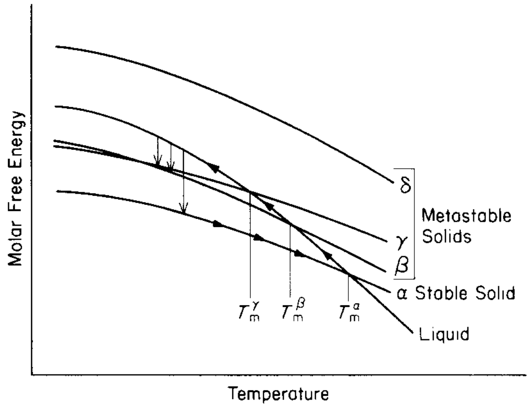

Fig. 1. Free energy *vs.* temperature curves illustrating possible free energy changes during heating and cooling cycles for a one-component system.

Examples of metastable melting were examined in detail for pure Ga [4]. The formation of a metastable solid of Ga can be attained quite easily by cooling liquid Ga droplets dispersed in oil. Droplets of liquid metal (less than several tens of micrometres) can be undercooled considerably relative to the melting point of the stable phase, T_m. The limit of undercooling depends on the crystal structure of the stable phase. When the stable crystal phase has a simple crystal structure, the limit of undercooling, which is determined by the homogeneous nucleation frequency of the solid phase, is about $0.2T_m$ [5]. In the case of Ga, which has a complex crystal structure, an undercooling of roughly $0.45T_m$ can be attained quite easily. Solidification with large undercooling generates various metastable solid phases in preference to the stable solid phase owing to Ostwald's step rule [6]. These metastable solid phases, still dispersed in oil, melt on heating at T_m values specific to each crystal structure. Successive melting of these metastable phases can be monitored experimentally by various methods (Fig. 2). Bosio *et al.* [4] have reported the free energy relations of several metastable and stable phases of Ga (Fig. 3). Metastable melting of a metastable solid phase was also reported for Bi [7], and for the stoichiometric intermetallic

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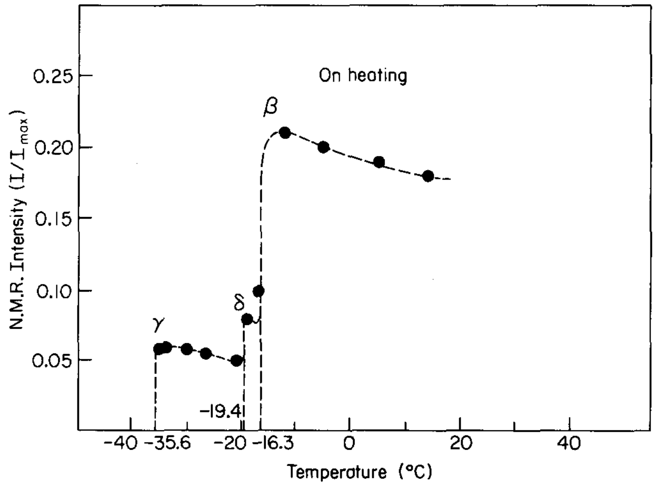

Fig. 2. Successive melting of metastable phases monitored by nuclear magnetic resonance spectroscopy. NMR intensity corresponds to the amount of liquid phase.

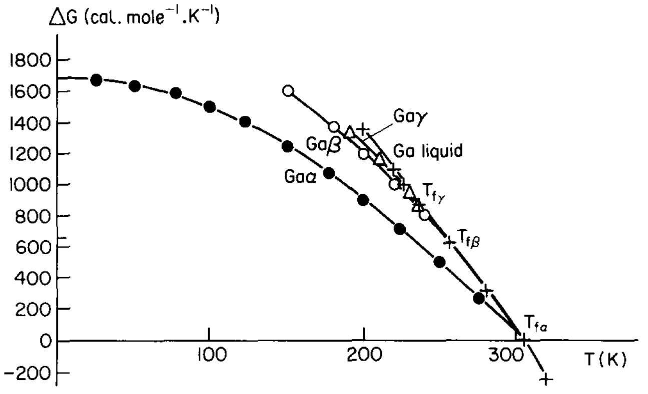

Fig. 3. Free energy relations of metastable and stable phases of Ga. ●, Gaα; ○, Gaβ; △, Gaγ; Ga liquid.

compound InBi [8]. In these cases, the metastable phases formed by solidification were found to be the stable phases at high pressure.

The interpretation of solid state amorphization as thermodynamically equal to metastable melting is clearly demonstrated by high-pressure experiments on ice [9]. The application of pressure to ordinary ice at 77 K causes amorphization at the pressure which matches the extension of the liquidus line in the *P–T* diagram as shown in Fig. 4. Figure 5 shows the measured volume change due to amorphization of ice by metastable melting. The melting of ice by the application of pressure is a natural phenomenon since ice is less dense than water. However, the experimental observation that such melting can take place metastably at temperatures at which the transition may be called amorphization is surprising.

Earlier, systematic investigations of metastable melting using high pressure have been reported for many semiconductor compounds by Ponyatovski *et al.* [10]. They reported that when the semiconductor phases were prevented from transforming into high-pressure metallic phases, transition into the amorphous phase by metastable melting occurred. Furthermore, they reported that when the high-pressure metallic crystalline phases, which can be retained at ordinary pressure by lowering the temperature, were heated at ordinary pressure, solid state amorphization took place by metastable melting. On further heating, these amorphous phases crystallized into the stable semiconductor compounds.

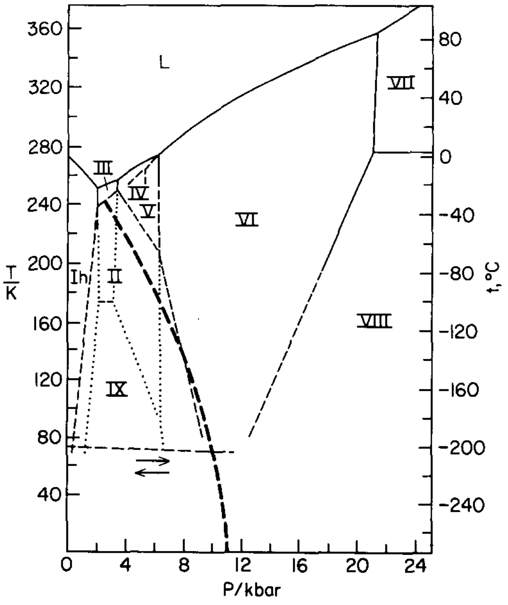

Fig. 4. Pressure–temperature diagram of H_2O.

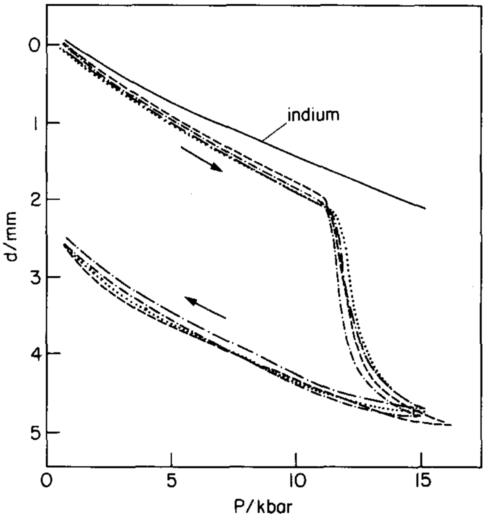

Fig. 5. Volume change due to amorphization of ice by metastable melting. Indium was used for pressure calibration.

The spontaneous amorphization of a crystalline phase has also been reported for the Se–Te alloy [11]. The Se–Te system has a simple phase diagram of complete solid solubility. Mushiage *et al.* [11] prepared an amorphous phase by rapidly quenching the liquid alloy of Se_{80}–Te_{20}. The application of high pressure at room

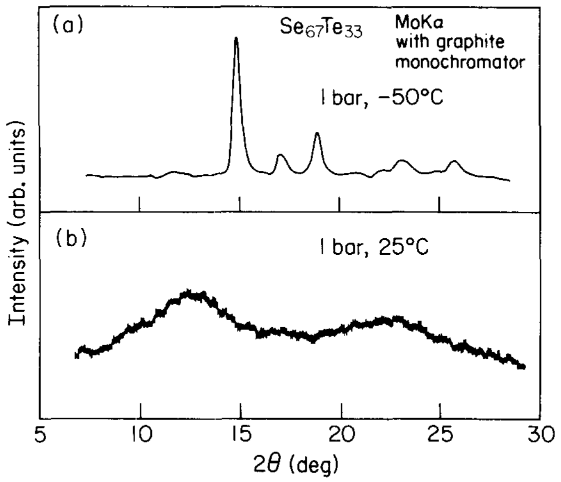

Fig. 6. Spontaneous amorphization of crystalline SeTe phase.

temperature to the amorphous Se_{80}–Te_{20} sample produced a crystalline metallic phase at about 100 kbar. The temperature was then lowered to 77 K. The reduction of pressure at this temperature did not destroy the high-pressure crystalline phase. When the temperature was raised to room temperature, spontaneous amorphization, as shown in Fig. 6, took place, which may be interpreted as metastable melting. They reported that the amorphous phase produced by liquid quenching could be repeatedly crystallized and reamorphized by pressurization and depressurization.

3. Metastable melting of alloys

The melting phenomenon of metastable crystalline phases below the melting temperature of the stable phase can also be observed for multiphase substances. The metastable eutectic reaction in the Fe–C system is a good example of such a phenomenon. The Fe–C system exhibits a typical "double diagram", having two eutectic reactions. By convention, the stable γ-graphite eutectic reaction is drawn by broken lines and the metastable γ-Fe_3C reaction is drawn by full lines. Ozaki *et al.* [12] demonstrated, by careful thermal analysis combined with examination of the metallographic structure of quenched samples, that the γ-Fe_3C sample partially melts by the metastable eutectic reaction at about 10 K lower than the γ-graphite sample. The partial phase diagram of the Fe–C system given by Ozaki *et al.* [12] and the corresponding thermal analysis data are shown in Fig. 7.

Similar to the case of single-phase substances described in the preceding section, the droplet undercooling technique can generate various metastable phases which melt at temperatures far below the stable melting reactions. An example of such a metastable phase diagram for Au–Sn, in which metastable eutectic melting was reported at 47 K below the stable eutectic temperature, is given in Fig. 8 [13].

When such metastable eutectic reactions lie far below the stable melting temperature, metastable eutectic melting may be observed as a solid state amorphization reaction. A schematic drawing of such a metastable eutectic reaction at very low temperature is shown in Fig. 9. The metastable phase diagram shown in Fig. 9 is typical of a system with a deep metastable eutectic reaction [14]. It should be noted that, as demonstrated clearly in Fig. 9 such a deep metastable eutectic reaction typically occurs for systems with one or more intermetallic compounds with very high melting temperatures.

Therefore we may expect the occurrence of solid state amorphization by the metastable eutectic reaction, as in Fe–C and Au–Sn systems, provided that the stable intermetallic compound formation can be suppressed. The starting multiphase substances in these cases are the mixtures of two phases of elements A and B given in Fig. 9.

4. Solid state amorphization by mechanical alloying

As stated clearly by Miedema and coworkers [15], a solid macroscopic mixture of two or more elemental metals often has a very high free energy relative to the intermetallic compound. This free energy difference, which roughly equals the enthalpy difference in the case of a solid state reaction, is often high enough to be utilized for the self-propagating, high-temperature synthesis (SHS) of intermetallic compounds [16]. The relative free energy state of the liquid alloy phase, which is a mixture at the atomic scale, may be much lower than the free energy state of the macroscopic mixture of the elements.

Figure 10(a) shows a schematic diagram of the free energy relation between the stable and metastable phases shown in Fig. 9. The temperature used to draw Fig. 10(a) is above the metastable eutectic line and below the stable eutectic line. In Fig. 10(a), the free energies of the solid phases of the pure elements A and B are taken as the reference state. Hence the free energy of the macroscopic mixture of these elements at any composition is represented as the straight horizontal line connecting the zero values in Fig. 10(a). The free energy of the liquid phase, which should be roughly equal to that of the amorphous phase, is lower than the horizontal line between the points *a*′ and *b*′. Consequently, the free energy hierarchy allows complete solid state amorphization to occur by metastable melting of the macroscopic solid mixture of elements A and B in this composition range. The trace of these equi-free energy points for the liquid and the mixture of

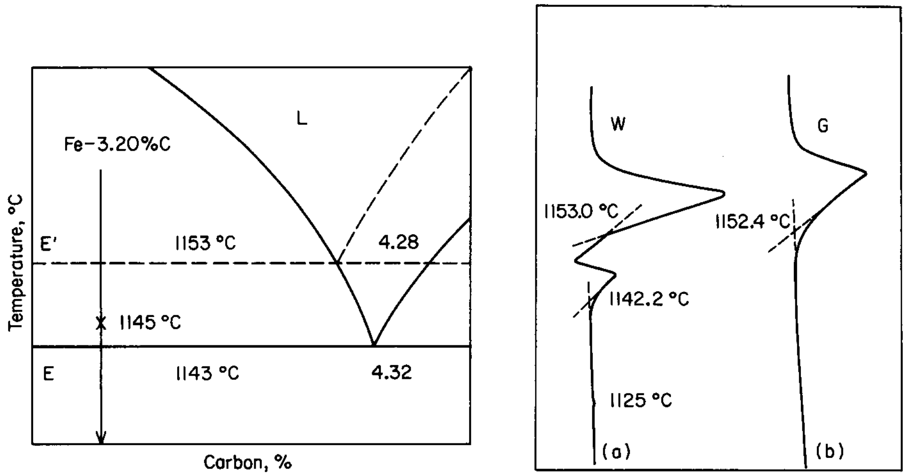

Fig. 7. Partial phase diagram of the Fe–C system and thermal analysis data. W and G refer respectively to white and gray cast iron.

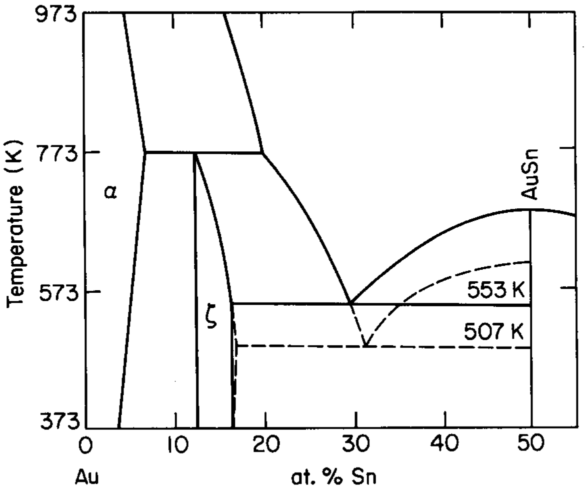

Fig. 8. Estimated metastable phase diagram of Au–Sn superimposed on the equilibrium phase diagram.

two elements (the trace of points a' and b' with the change in temperature) may be called the T_0 curve for solid state amorphization.

In Fig. 10(b), the T_0 line is given, together with the extension of the liquidus line which forms the metastable eutectic phase diagram. It should be noted that even in the ranges outside the T_0 line, partial amorphization from the macroscopic solid mixture of the two elements is possible. The coexistence of the amorphous phase and the terminal solid solution has a lower free energy state than the horizontal line, as shown by the broken lines drawn as the tangents to the relevant free energy curves (Fig. 10(b)).

Amorphization by a solid state reaction does not usually take place by simply mixing two pure elements in the solid state, for instance by placing powders of two elements together in a vial. In order for amorphization to take place in the solid state, it is necessary to mix two pure elements on an extremely fine scale. Artificial multilayer deposition of two elements from the vapour phase can produce such a condition.

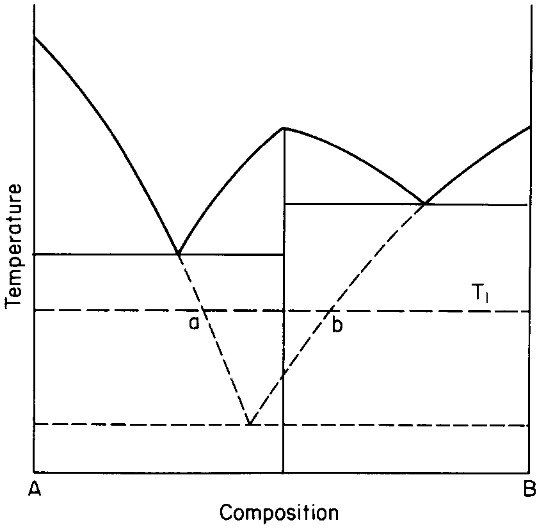

Fig. 9. Schematic phase diagram of a "deep metastable eutectic" system. The glass forming ability (GFA) may be large in the metastable eutectic composition range. If temperature T_l is near the glass temperature T_g, the "metastable melting" of elements A and B in an alloy concentration range between a and b may be considered as "solid state amorphization".

An example was reported by Schwarz and Johnson [17] for the solid state amorphization of an Au–La multilayer sample. This system has several high-melting-temperature intermetallic compounds and the free energy of the metastable liquid lies far below that of the mixture of pure Au and La solid phases.

Mechanical alloying, which was first developed for the production of oxide-dispersion-strengthened materials [18], provides an easy way to produce an extremely fine mixture of metallic and non-metallic elements in the solid state. The basic principle of this process is

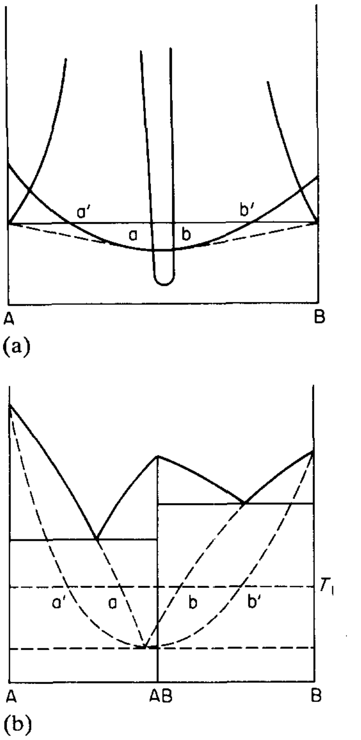

Fig. 10. (a) Free energy relation between the stable and metastable phases shown in Fig. 9. (b) T_0 curve for solid state amorphization.

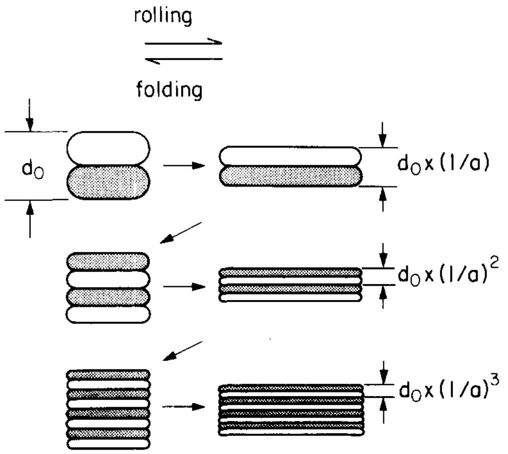

Fig. 11. Schematic explanation of particle size reduction by mechanical alloying.

the repetition of rolling and folding as illustrated in Fig. 11. When the reduction in thickness by one event of rolling is $(1/a)$, repeated rolling and folding for n times produces a fine lamination of two metals with the thickness of each layer being $(1/a)^n$ times the initial thickness.

Numerous studies of the change in metallographic structure by mechanical alloying have been performed. In almost all cases, extremely fine mixing of the starting elements has been reported (dimensions of several tens to 100 nm).

When an alloy system with metastable liquid free energy values lower than that of a mixture of the pure solid elements is mechanically alloyed to a very fine lamination, spontaneous amorphization may be expected by metastable melting at around room temperature. Most of the alloy systems in which amorphization has been reported, since the early work on the Ni–Nb system by Koch *et al.* [19], have a relatively large negative heat of mixing. A large negative heat of mixing implies the stabilization of the intermetallic compound and also of the metastable liquid phase, providing the possibility of a metastable melting reaction.

Figure 12 shows the free energies of various phases for the Al–Fe system drawn at 500 K [20]. Mechanical alloying by low-energy ball milling or by repeated rolling for the Al-rich composition range of this system produces the amorphous phase. The gradual increase in the fraction of the amorphous phase was monitored by Mössbauer spectroscopy as shown in Fig. 13 [21]. The Mössbauer spectra indicate that the amorphous phase starts to form at a very early stage of mechanical alloying. The mechanical mixing of atoms at the contact interface between the Al and Fe phases is the reason for such early amorphization. It should be noted that by the simple process of milling, amorphization readily takes place in this alloy system for which the amorphization by liquid quenching is difficult.

Mechanical alloying can even raise the free energy of the starting materials. Hence amorphization of a stable intermetallic compound by mechanical milling is possible [22]. The degree of elevation of the free energy by ball milling can roughly be estimated by measurement of the stored enthalpy. The ball milling of this system, starting from mixtures of the pure elemental powders of Ag and Cu, produced a complete solid solution f.c.c. phase for all compositions [23]. The free energy of the liquid phase in this system is only

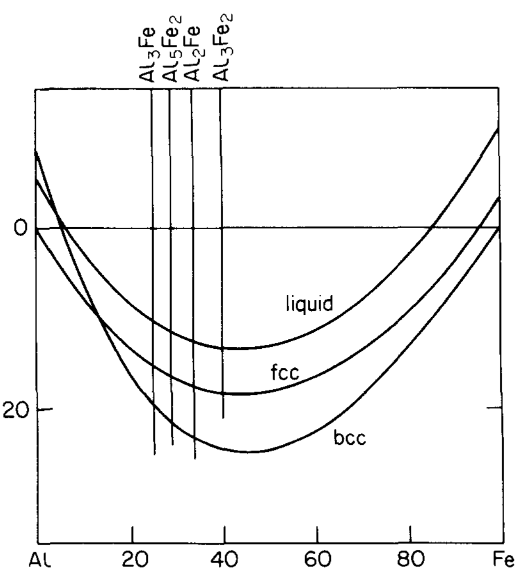

Fig. 12. Free energies of phases in the Al–Fe system at 500 K.

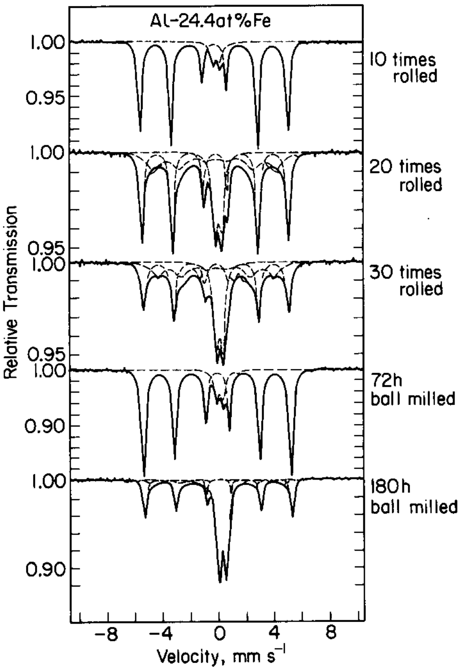

Fig. 13. Increase in the fraction of the amorphous phase in the Al–Fe system monitored by Mössbauer spectroscopy.

several kilojoules per mole higher than the excess energy stored in the metastable supersaturated solid solution phase. Thus solid state amorphization by metastable melting may be possible not only for systems with a negative free energy of mixing but also for systems with a small positive free energy of mixing by the method of mechanical alloying. An example of such a case has recently been reported for the Cu–Ta system [24].

5. Conclusions

When a powdered mixture of Sn ($T_m = 505$ K) and Pb ($T_m = 600$ K) melts at the eutectic temperature of 456 K, it is not surprising. However, when an artificial multilayer of Au ($T_m = 1336$ K) and La ($T_m = 1085$ K) amorphizes at 673 K, this is deemed to be unusual. As illustrated in Fig. 9 these two phenomena are thermodynamically the same eutectic melting reaction. The latter example appears unusual because we are not accustomed to commonly observing metastable reactions. Metastable reactions are common in low-temperature solid state reactions because of the Ostwald step rule [6] and also because of the low atomic mobility which may suppress the formation of the stable phase.

Mechanical alloying is a simple process of repeated rolling and folding. Yet, it can readily realize, in almost any combination of materials, solid state mixing to a nanometre size range. Almost unbound possibilities of metastable reactions have yet to be explored, including many new metastable melting processes or solid state amorphization.

References

1 D. Turnbull, *Metall. Trans. A, 12* (1981) 695.
2 T. P. Seward III, in A. M. Alper (ed.), *Phase Diagrams,* Academic Press, New York, 1970, p. 295.
3 J. C. Baker and J. W. Cahn, *Solidification,* American Society for Metals, Metals Park, OH, 1971, p. 23.
4 L. Bosio, R. Cortes and A. Defrain, *J. Chem. Phys., 70* (1973) 357.
5 D. Turnbull, *J. Appl. Phys., 21* (1950) 1022.
6 K. N. Ishihara, M. Maeda and P. H. Shingu, *Acta Metall., 33* (1985) 2113.
7 J. H. Perepezko, in R. Mehrabian, B. H. Kear and M. Cohen (eds.), *Rapid Solidification Processing,* Vol. II, Claitor's, Baton Rouge, LA, 1980, p. 56.
8 K. N. Ishihara, K. Mori and P. H. Shingu, in S. Steeb and H. Warlimont (eds.), *Rapidly Quenched Metals,* Elsevier, Amsterdam, 1985, p. 55.
9 O. Mishima, L. D. Calvert and E. Whalley, *Nature, 310* (1984) 393.
10 E. G. Ponyatovski, I. T. Belash and O. I. Barkalov, *J. Non-Cryst. Solids, 117/118* (1990) 679.
11 M. Mushiage, K. Tamura and H. Endo, *J. Non-Cryst. Solids, 59/60* (1983) 887.
12 R. Ozaki, H. Miyake and M. Okada, *J. Jpn. Foundrymen's Soc., 51* (1979) 327.
13 K. N. Ishihara, H. Gohchi and P. H. Shingu, in E. W. Collins and C. C. Koch (eds.), *Undercooled Alloy Phases,* TMS, Warrendale, 1986, p. 49.
14 P. H. Shingu, Mater. Sci. Eng., 97 (1988) 134.
15 F. R. deBoer, R. Boom, W. C. M. Mattens, A. R. Miedema and A. K. Niessen, *Cohesion in Metals,* Vol. 1, Elsevier, Amsterdam, 1988.
16 Z. A. Munir and U. Anselmi-Tambulini, *Mater. Sci. Rep., 3* (1989) 277.
17 R. B. Schwarz and W. L. Johnson, *Phys. Rev. Lett., 51* (1983) 415.
18 J. S. Benjamin, *Mater. Sci. Forum, 88–90* (1992) 1.
19 C. C. Koch, O. B. Cavin, C. G. Mckamey and J. O. Scarbrough, *Appl. Phys. Lett., 43* (1983) 1017.
20 P. H. Shingu, K. N. Ishihara, K. Uenishi, J. Kuyama, B. Huang and S. Nasu, in A. H. Clauer and J. D. de Barbadillo (eds.), *Solid State Powder Processing,* TMS, Warrendale, 1990, p. 21.
21 S. Nasu, S. Imaoka, S. Morimoto, H. Tanimoto, B. Huang, T. Tanaka, J. Kuyama, K. N. Ishihara and P. H. Shingu, *Mater. Sci. Forum, 88–90* (1992) 569.
22 R. B. Schwarz and C. C. Koch, *Appl. Phys. Lett., 49* (1986) 146.
23 K. Uenishi, K. F. Kobayashi, K. N. Ishihara and P. H. Shingu, *Mater. Sci. Eng., A134* (1991) 1342.
24 C. H. Lee, T. Fukunaga and U. Mizutani, *Mater. Sci. Eng., A134* (1991) 1334.