MECHANOCHEMISTRY AND MECHANICAL ALLOYING 2003

JOURNAL OF MATERIALS SCIENCE **39** (2004) 5461–5465

Mechanical alloying of Fe-transition metal systems: The analysis of different stages

I. V. POVSTUGAR*, P. YU. BUTYAGIN
N. N. Semenov Institute of Chemical Physics, 4 Kosygin str., Moscow 119991, Russia
E-mail: str@center.chph.ras.ru

The paper presents the results of the quantitative analysis of mechanical alloying (MA) in binary systems Fe-X (X = Ti, Zr, Nb, Mo, Ta, W). MA has been studied as a sequence of interrelated microscopic processes (structural refinement of initial components, consumption of Fe and X, transition of atoms into alloying products) by means of X-ray diffraction analysis, Mössbauer spectroscopy and thermomagnetic measurements. The evolution of the systems in the process of MA in terms of their structure and composition has been described as the function of the quantity (dose) of mechanical energy supplied to the mixture. © *2004 Kluwer Academic Publishers*

1. Introduction

Mechanochemical synthesis (called *mechanical alloying* in case of metals), in contrast to ordinary chemical reactions, is a non-thermal process controlled by the quantity of mechanical energy absorbed. Therefore, one of the fundamental tasks in the process of its study is to investigate the paths of transformation of the absorbed mechanical energy as well as the mechanisms responsible for mass transfer and structural-phase transformations under intense mechanical treatment.

Binary iron-containing systems, namely, Fe-X (X = Ti, Zr, Nb, Mo, Ta, W) with the component ratio 80:20 at.% were taken as model samples. In this case it is possible to obtain detailed information on the MA process using Mössbauer spectroscopy and thermomagnetic measurements. The results of MA kinetics studies for several systems are given in our previous work [1–4]. Similar investigations have been performed by other authors: Fe-Ti [5, 6], Fe-Zr [7–11], Fe-Nb [12–14], Fe-Mo [15], Fe-Ta [16, 17], Fe-W [18–22].

MA was considered as a sequence of interrelated processes, such as structural refinement of mixture components, loss of atoms from initial component phases etc., caused by mechanical energy absorption under mechanical treatment. The depth at which the processes took place was correlated with the quantity of the energy supplied (dose D, J/g_{mixture}).

2. Experimental

Powder mixtures of pure Fe and X (X = Ti, Zr, Nb, Mo, Ta, W) were mechanically treated at room temperature under Ar atmosphere in a vibration ball mill, with the stainless steel vial and balls from ball-bearing steel. The vial was water-cooled to avoid mixture heating. The energy intensity of the mill was 1.0–3.5 W/g. The relative level of contamination of the mixtures with the material of the milling tools was $\leq 1\%$. X-ray diffraction, ^{57}Fe Mössbauer spectroscopy and thermomagnetic measurements were used to study the phase composition and structural parameters of the systems. The values of coherent scattering range $\langle L \rangle$, set equal to grain sizes, were calculated using Williamson-Hall method.

3. Results and discussion

The MA begins with the refinement of components crystalline structure, which is accompanied by the consumption of their phases, i.e., by the decrease of the number of Fe and X atoms composing these phases. Further mechanical treatment results in the formation of the products and their following structural transformations. Let us consider some processes in more detail.

3.1. Structural refinement of initial components

At the beginning of mechanical treatment of the mixtures the grain sizes of the initial components decrease to the value of $\sim$10 nm, i.e., the systems pass into nanocrystalline state. It is convenient to characterize the depth of structural refinement via the specific area of intergrain boundaries of the components, S (m^2/g). The value of S is calculated with the account of grain sizes $\langle L \rangle$: with the cubic shape of crystalline blocks with an $\langle L \rangle$ edge, the intergrain boundaries area makes $S = 3/(\rho \cdot \langle L \rangle)$, where ρ is the material density.

Fig. 1 presents the areas of intergrain boundaries of α-Fe phase at different stages of mechanical treatment of Fe(80)X(20) mixtures; data on the mechanical grinding of pure Fe [3] are also plotted for comparison. At doses up to 10–20 kJ/g, S increases proportionally to the dose, and the value of $A_S = D/S$ can be defined as the work

---

*Author to whom all correspondence should be addressed.

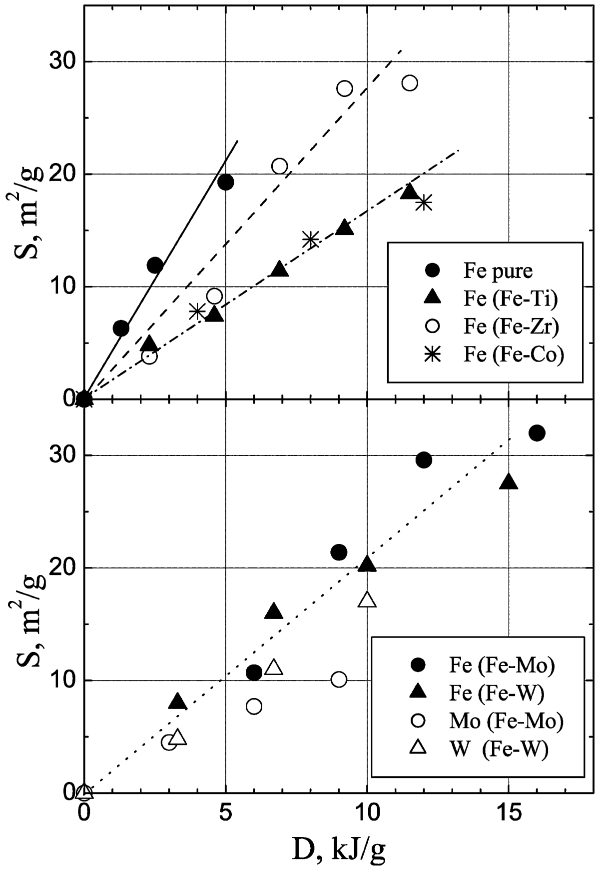

Figure 1 The dependence of specific area of intergrain boundaries S on dose D. The similar dependence for the case of the grinding of pure Fe is also plotted.

of intergrain boundaries formation. Table I presents the results for the A_S for the mixtures studied. One can see that in the Fe-X systems the value of A_S is greater than in pure Fe. It means that the addition of a second metal to iron hinders Fe structural refinement. The value of A_S makes up several hundreds of J/m^2 on average, which is two-three orders of magnitude higher than surface energy of pure metals.

The calculation of the area of intergrain boundaries of X component is usually hindered because of a low X content in the mixture and a resulting rather low intensity of the corresponding diffraction lines. Satisfactory data were only obtained for Fe-W and Fe-Mo (see Fig. 1). It is seen that in these systems, the dynamics of the Mo and W intergrain boundaries area changes is similar to that of Fe, i.e., in both components structural refinement occurs simultaneously.

TABLE I The work of intergrain boundaries formation (A_S), the yield of formation of iron boundary atoms G_S(Fe), the energy yield of X phase consumption $G(-X)$, and the yield of initial X accumulation for various Fe-X systems

System	A_S (J/m^2)	G_S(Fe) (mol/MJ)	$G(-X)$ (mol/MJ)	$G(+X)$ (mol/MJ)
Fe	230	0.12	–	–
Fe-Sn			0.6	0.07
Fe-Ti	640	0.04	0.26	0.03
Fe-Zr	350	0.08	0.35	0.03
Fe-Nb			0.16	0.15
Fe-Ta			0.12	0.12
Fe-Mo	440	0.06	0.07	0.07
Fe-W	460	0.06	0.05	0.05

In the materials, in which deformation is developing following a plastic mechanism (namely, in metals), the main part of energy absorbed by a material at the initial stage of mechanical treatment is consumed in the processes of nucleation and migration of dislocations. Later on, in the process of dislocations alignment, a net of intergrain boundaries is formed, which is characterized by the grain structure size. Let us consider this process using the structural refinement of pure Fe as an example.

Every step of a dislocation line displacement for one lattice parameter is accompanied by the energy $E_1 = \sigma \cdot \upsilon_0$ consumption per one atom on this line (σ is the yield strength of the material, υ_0 is its atomic volume). For iron $\sigma = 1.7 \times 10^8$ Pa, $\upsilon_0 = 1.2 \times 10^{-29}$ m^3, and $E_1 \approx 2 \times 10^{-21}$ J. At the very beginning of mechanical treatment the size of nanocrystalline blocks L is approximately 1 μm by order of magnitude, i.e., $L \approx 10^4$ lattice parameters; that distance should be passed by a dislocation before it comes into a boundary. The surface atomic density at intergrain boundaries N_S is about 10^{19} atoms/m^2. In proposition that every atom at intergrain boundaries is incorporated into a dislocation line, we can assume the amount of work spent on movement of dislocations that subsequently formed intergrain boundaries:

$$A = E_1 \cdot L \cdot N_S \approx 10^2\ \mathrm{J/m^2}$$

(the accuracy of the estimations given lies within the limits of one order of magnitude). As one can see, this value is in a good agreement with the experimental A_S values. Thus, the formation of intergrain boundaries in metals requires the energy consumption of hundreds of J/m^2, which is experimentally observed.

3.2. Consumption of initial component phases

Simultaneously with structural refinement of the components at the initial stage of mechanical treatment, the phases of one or both initial components of the mixture are consumed. Fig. 2 demonstrates the dependence of X phase consumption on the dose D obtained using X-ray diffraction. It is seen that the dependence is close to linear, with the slope of line reflecting the molar energy yield of X phase consumption—$G(-X)$:

$$G(-X) = -\frac{\delta D}{\delta X}, \quad \mathrm{mol/MJ}.$$

The assessed values of $G(-X)$ are given in Table I. Also, a $G(-X)$ value for Fe(68)Sn(32) is presented, which was calculated based on the data from [23].

The yield of X phase consumption (i.e., the value of $G(-X)$) can be compared with the yield of formation of iron boundary atoms G_S(Fe) in a corresponding system Fe-X. G_S(Fe) yield can be determined as the molar quantity of Fe atoms that can be located as

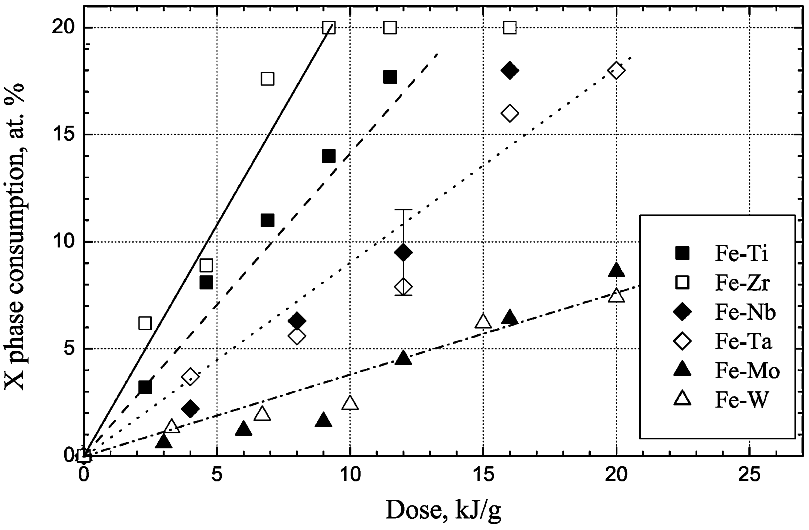

Figure 2 Consumption of X phase against dose.

one layer along its intergrain boundaries (see Table I). The $G(-X)$) value for Fe-Ti and Fe-Zr is several times higher than the value of G_S(Fe), while for Fe-Mo and Fe-W these yields are approximately the same.

The structural evolution of materials under mechanical treatment is determined by their response to the mechanical loading applied. Therefore, the rate of the initial components consumption should depend on their mechanical characteristics. Indeed, there is a correlation between the value of $G(-X)$ and the yield strength of the X metal (Fig. 3): in case the yield strength increases, the yield $G(-X)$ for a corresponding system drops. Hence, one can conclude that the rate of X phase consumption characterized is determined by the degree of readiness, with which metal X converts into a plastic flow state.

3.3. Transition of atoms into MA products

Beginning with the second stage, structural refinement and initial components consumption under mechanical treatment are accompanied by mass transfer, which causes the formation of MA products, which composition and structure can considerably change during alloying process. Based on the results of the quantitative phase analysis, performed using the data of X-ray diffraction analysis and Mössbauer spectroscopy, it became possible to determine both the quantity of the consumed X phase and the quantity of the X atoms that had passed into MA products.

The systems examined can be divided into two groups. In Fe-Ti and Fe-Zr systems there is a noticeable delay between the consumption of X phase and accumulation of X atoms in the products (see Fig. 4A with Fe-Ti as an example). In other systems X atoms pass into products without any delay (see Fig. 4B with Fe-W as an example). Let us examine the process of MA products formation separately for each group.

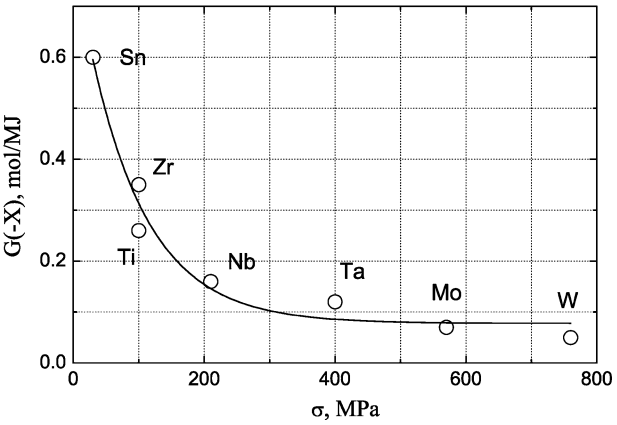

Figure 3 Correlation between yield strength σ of the X metal and yield of X consumption $G(-X)$.

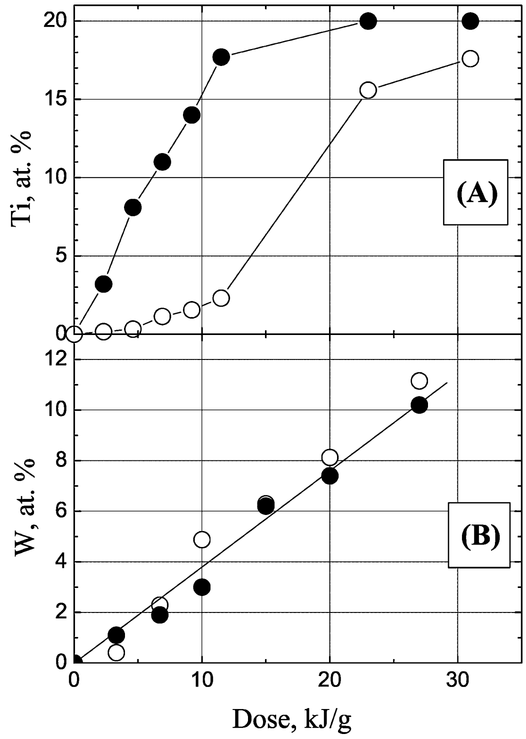

Figure 4 Comparison of X consumption (solid symbols) and transition of X into MA products (open symbols): Fe-Ti (A) and Fe-W (B).

3.3.1. Fe-Ti and Fe-Zr systems

These systems are characterized by quick consumption of the X phase ($G(-X) > 0.2$ mole/MJ) at a comparatively slow transition of X atoms into the products. The delay between these processes evidences the accumulation of X atoms in a certain intermediate state, representing small clusters or rather thin "films" (1 nm at most), which, therefore, cannot be registered by X-ray diffraction analysis. This implies that at the initial stage of MA X atoms spread along the α-Fe grain boundaries and form intergrain interlayers. Assuming that X component is uniformly distributed along the intergrain boundaries, the thickness of these interlayers can be assessed from above by correlating the yield of $G(-X)$ with the yield of the boundary iron atoms formation $G_S(\mathrm{Fe})$:

$$N \approx \frac{G(-X)}{G_\mathrm{S}(\mathrm{Fe})}$$

where N is the interlayer thickness in the number of X component monolayers. The calculation using this relation gives a value of no more than 6–7 monolayers, that is ≤ 1 nm. The layers of this thickness should only contribute to the diffuse background on X-ray diffraction patterns and will not give clear lines, which is an actual reason for the experimentally observed decrease of X phase content without the transition of X atoms into the alloying products. The effect of the segregation of one component along the intergrain boundaries of the other was also discovered during the MA of binary mixtures of iron with a set of sp-elements [24].

As the dose increases, the intense formation of the alloying products occurs. Namely, the supersaturated solid solution of αFe(Ti) is formed in Fe-Ti system, and the amorphous phase $Fe_{73}Zr_{27}$ with a constant (up to a dose of 25 kJ/g) composition is formed in Fe-Zr system. The products presumably form due to Fe and X atoms interaction at the contact boundary of crystallites and intergrain interlayers.

MA in Fe-Ti and Fe-Zr systems has well pronounced stage behavior. The initial stage is characterized by transition of the systems into nanocrystalline state; the X phase here virtually disappears. Only as soon as these processes are completed, the intense formation of the alloying products begins. The degree of the manifestation of the stage behavior can be expressed via a correlation between the yield of consumption, $G(-X)$, and the yield of initial X accumulation in MA products, $G(+X)$, which is defined similarly to $G(-X)$. The case with $G(-X) \gg G(+X)$, which takes place with Fe-Ti and Fe-Zr systems (see Table I) corresponds to pronounced stage behavior of MA.

3.3.2. Fe-Nb, Fe-Mo, Fe-Ta and Fe-W systems

The initial product of MA is a solid solution of α-Fe(X), which is formed as early as the dose of 3–4 kJ/g is supplied. Both residual pure Fe and solid solution are present in the mixture in this case. The concentration of the solid solution and its phase content in the Fe-Mo and Fe-W mixtures grow monotonously with the dose. With the dose of 12 kJ/g, supplied to the Fe-Nb and Fe-Ta systems, the amorphous phase appears.

In this case the consumption of X phase and the transition of X into MA products proceed simultaneously, i.e., no accumulation of X at the Fe intergrain boundaries occurs. It is quantitatively reflected as the equality $G(-X) \approx G(+X)$ (Table I). For the systems examined the accumulation of X in the products is proportional to the dose (see Fig. 4) practically along the whole MA process. Accordingly, the process of MA for the case of $X =$ Nb, Mo, Ta, W does not have pronounced stage behavior; the product begins to form as early as the low doses are applied, and proceeds with a permanent yield.

It is noteworthy, that pronounced stage behavior of MA is observed in the systems with a rather large value of $G(-X)$. It can thus be concluded that in the case of the intense consumption of X phase, the limiting stage of MA is the transition of X atoms from the intermediate state (grain boundary interlayers) into the product phases. In contrast, if the systems have a low $G(-X)$ yield, it is almost impossible to separate the alloying stages, because after X atoms leave their own lattice, they pass into the products. In this case the consumption of the initial components serves as the limiting stage of MA. Thus, there are two different cases ($X =$ Ti, Zr and $X =$ Nb, Mo, Ta, W), in which the rate of product formation is governed by the completely different microscopic processes taking place in the course of MA.

4. Conclusions

MA in binary metal systems Fe-X ($X =$ Ti, Zr, Nb, Mo, Ta, W) has been considered as a sequence of microscopic processes. The efficiency of mixture structural refinement under mechanical treatment can be conveniently characterized by the work of intergrain boundaries formation A_S for the initial components. The values of A_S have been estimated and it has been shown that energy supplied is predominantly spent on dislocations migration. The energy yields of X consumption, $G(-X)$, and the initial energy yields of X accumulation in MA products, $G(+X)$, have been assessed. The correlation between the yield of X consumption and the yield point of a corresponding X metal has been found.

MA has a pronounced stage behavior if $G(-X) \gg G(+X)$: the initial stage (Fe and X structural refinement, consumption of the X phase) and the stage of MA products formation are clearly separated, the accumulation of X atoms along Fe intergrain boundaries occurs, and the limiting stage of MA is the transition of X atoms from intergrain interlayers into products. In the systems with $G(-X) \approx G(+X)$ no accumulation of X atoms along Fe intergrain boundaries exists, as well as no pronounced stages are observed in the course of MA, and the yield of products formation is limited by the process of X phase consumption.

Acknowledgements

Authors are grateful to Prof. E. P. Yelsukov, Dr. A. N. Streletskii and Dr. G. A. Dorofeev for fruitful discussions. The work was supported by Russian Foundation for Basic Research, grant 01-03-32803.

References

1. I. V. POVSTUGAR, D. S. CHICHERIN, P. YU. BUTYAGIN and V. K. PORTNOI, *Coll. Journ.* **62** (2000) 412.
2. I. V. POVSTUGAR, P. YU. BUTYAGIN, G. A. DOROFEEV and E. P. ELSUKOV, *ibid.* **64** (2002) 178.
3. I. V. POVSTUGAR, E. P. ELSUKOV and P. YU. BUTYAGIN, *ibid.* in press.
4. *Idem.*, *ibid.* **65** (2003) 178.
5. A. A. NOVAKOVA, O. V. AGLADZE, S. V. SVESHNIKOV and B. P. TARASOV, *Nanostruct. Mater.* **10** (1998) 365.
6. T. A. POPOVICH, O. V. ARESTOV, A. A. POPOVICH and A. S. KUCHMA, *J. Mater. Sci. Techn.* **17** (2001) 1.
7. L. SCHULTZ and J. ECKERT, *Topics in Appl. Phys.* **72** (1994) 69.
8. N. BURGIO, A. IASONNA, M. MAGINI, S. MARTELLI and F. PADELLA, *Il Nuovo Cimento* **13D** (1991) 459.
9. A. W. WEEBER and H. BAKKER, *Physica* B **153** (1988) 93.
10. S. E. LEE, H. Y. RA, T. H. YIM and W. T. KIM, *Mater. Sci. Forum* **179–181** (1995) 121.
11. R. PIZARRO, J. S. GARITAONANDIA, F. PLAZAOLA, J. M. BARANDIARAN and J. M. GRENECHE, *J. Phys.: Condens. Matter* **12** (2000) 3101.
12. M. S. EL-ESKANDARANY, A. A. BAHGAT, N. S. GOMAA and N. A. EISSA, *J. Alloys Compd.* **290** (1999) 181.
13. J. I. YANG, T. J. ZHANG, K. CUI, X. G. LI and J. ZHANG, *ibid.* **242** (1996) 153.
14. C. K. LIN, P. Y. LEE, S. W. KAO, G. S. CHEN, R. F. LOUH and Y. HWU, *Mater. Sci. Forum* **312–314** (1999) 55.
15. E. JARTYCH, M. KAROLUS, D. OLESZAK, J. K. ZURAWICZ, J. SARZYNSKI and M. BUDZUNSKI, *J. Alloys Compd.* **337** (2002) 69.
16. C. K. LIN, P. Y. LEE, J. L. YANG, C. J. TUNG, N. F. CHENG and Y. K. HWU, *J. Non-Cryst. Solids* **232–234** (1998) 520.
17. M. MERTINAT, U. HERR, D. OELGESCHLAGER and K. SAMWER, *J. Appl. Phys.* **85** (1999) 3512.
18. T. D. SHEN, K. Y. WANG, M. X. QUAN and J. T. WANG, *ibid.* **71** (1992) 1967.
19. G. LE CAER, P. DELCROIX, T. D. SHEN and B. MALAMAN, *Phys Rev.* B **54** (1996) 12275.
20. HAI YANG BAI, C. MICHAELSEN, W. SINKLER and R. BORMANN, *Mater. Sci. Forum* **235–238** (1997) 361.
21. M. KIS-VARGA, D. L. BEKE and L. DAROCZI, *ibid.* **343–346** (2000) 841.
22. E. JARTYCH, J. K. ZURAWICZ, D. OLESZAK and M. PEKALA, *J. Magn. Magn. Mater.* **218** (2000) 247.
23. G. A. DOROFEEV, G. N. KONYGIN, E. P. YELSUKOV, I. V. POVSTUGAR, A. N. STRELETSKII, P. YU. BUTYAGIN, A. L. ULYANOV and E. V. VORONINA, in “Mössbauer Spectroscopy in Materials Science,” 1999, edited by M. Miglierini and D. Petridis (Kluwer Academic Publishers, Netherlands, 1999) p. 151.
24. E. P. YELSUKOV, G. A. DOROFEEV and V. V. BOLDYREV, *Doklady Chimii* **391** (2003) 206.

Received 11 September 2003
and accepted 27 February 2004