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Influence of crystal structure on mechanical activation effect①

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Abstract: The effect of mechanical treatment on pyrite and molybdenite was studied. After mechanically activated for 40 min under the same condition, the apparent activation energy for leaching reaction of layer-structured molybdenite in HNO_3-H_2SO_4 solution becomes 6.0 kJ/mol lower than that for untreated one; while for isotropic pyrite, this value is 18.3 kJ/mol. Pyrite seems to be more sensitive towards mechanical activation. Resorting to the difference in crystal structure, it is considered that anisotropic molybdenite may obviate violate mechanical action through inter-layer slippage, while isotropic pyrie can not. So the action may damage pyrite crystal and produce large amount of lattice imperfection. Consequently, more mechanical energy is absorbed by pyrite crystal. So it is one-sighted to consider the mechanical activation effect according to only crystal lattice energy. Crystal structure, isotropy or anisotropy, is an important parameter which affects a lot.

Key words: mechanical activation; crystal structure; apparent activation energy

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1 INTRODUCTION

It is well acknowledged that intense mechanical action may cause remarkable increase in reactivity of solids. A lot of basic research in fields of geology[1], metallurgy[2-6], as well as chemical engineering[3], has shown that pressure and stress are concentrated at the contact sites. Depending on the characterization of solids and mode of mechanical action(compressive stress or shearing stress), the energy of stress field can spread over the neighbouring regions of the crystal through various processes. When the stress exceeds a critical value, crystal will crack and form new surface. The interesting phenomena is that under even more intense stress when critical time for forming crack becoming shorter than the mechanical action time, or the size of particle that suffering stress becoming less than the critical geometric size for forming crack, plastic deformation will come into existence and cause accumulation of various lattice imperfection. Succeedingly, mechanical energy is transformed into chemical one and is stored in crystal. Such process that causing increase in the energy level, and correspondingly chemical reactivity, is called mechanical activation(MA)[4, 7].

At present MA has been applied in extractive metallurgy successfully. For example, the thermal mill process developed by chinese researchers has been widely adapted by most of the domestic tungsten companies[8, 9]. This caustic soda process enables us to digest various kinds of tungsten ore, including scheelite that is considered by oversea metallurgists to be very refractory towards NaOH[10]. We also published our work on MA and leaching of pyrite[11, 12], chalcopyrite[13], sphalerite[14] and monazite[15]. A great sum of papers reported about enhancing pyro- or hydro-metallurgical processes as well as materials science[16-18].

But heretofore most work still keeps topically, without a bird-eye view of the whole subject. Many a time, certain engineering parameter such as catalyst efficiency[19], sintering behavior[20] or leachability[11], is studied with certain solid material or by certain MA method. Owing to the lacking of comparability, it is difficult to extract the regularity behind various works. Practice have shown that there are not universal conditions for MA. Many potential parameters, for instance, equipment, atmosphere, chemical bond of solid as well as morphology, may influence the effect of mechanical activation.

The impact of mill style and atmosphere(dry or wet milling) on pyrite activity in HNO_3-H_2SO_4 solution have been extensively described elsewhere[11]. Criado et al[21] studied the influence of MA on thermal decomposition of alkaline earth carbonates. The activation effect is evaluated by the change of apparent activation energy for chemical reaction. It is found that the lower the lattice energy of carbonates, the better the activation effect is. These re-

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sults is helpful for deepening understanding about the regularity for MA of different substance. But profound regularities may still be enshrouded in mist since the minerals they used are of different crystal structure, although the minerals are of the same alkaline earth oxy-salt.

Our initial research on the causality of crystal structure and MA is reported in this paper.

2 EXPERIMENTAL

The compositions of pyrite and molybdenite used are listed in Table 1 and Table 2, respectively.

Table 1 Chemical composition of pyrite used

Element	Fe	S	SiO_2
w / %	44.67	51.57	2.12

Table 2 Chemical composition of molybdenite used

Element	Mo	S	SiO_2
w / %	51.53	34.54	1.53

The mass of material was measured and the material was put into *d* 7.0 cm × 6.0 cm pot set in a planetary ball mill with 500 g *d* 1.0 cm iron ball. And the MA treatment was carried out at a centrifugal acceleration of 980 m/s^2 at room temperature. 800 mL HNO_3-H_2SO_4 solution prepared from analytical grade reagents and distilled water was filled in a 1 000 mL flask with a glass stirrer and heated to desired temperature. The reaction was initiated by adding 5.0 g mineral to the solution. 1 mL liquor sample was withdrawn each time at certain time interval for determining leaching ratio through analyzing the Fe or Mo concentration. It is worthy emphasizing that the stirring speed was controlled at 400 r/min and was proved to be high enough for dispelling the effect of solution diffusion.

3 RESULTS AND DISCUSSION

3.1 Mechanical activation of pyrite

Fig. 1 shows the kinetic curves for leaching of non-activated pyrite sample. It appears that temperature affects leaching deeply. For instance, no more than 40% of Fe can be leached after 100 min at 50 ℃, but 80% of Fe can be leached within 20 min when temperature is increased to 90 ℃. As it can be seen that, at the beginning of leaching, there exists induction time which becomes longer when temperature decreases, and so makes the kinetic curves into a sigmoidal shape. This declares that the leaching of pyrite is self-catalytic. Owing to the lack of surface active site, the initial leaching rate, slop of tangent line, is slow. With the enlarging of old sites and creating of new ones through dissolving reaction, the leaching itself is gradually speeded up and becomes the fastest when the active area occupied the whole unreacted surface. After that time, leaching rate decelerates and gradually verges to zero with time as a result of shrinkage of reaction area. Since high temperature is favorite for the whole process, shrinkage or even disapperance of induction period can be seen when temperature increases. According to what is proposed in Ref. [22], Arrhenius plot is drown as Fig. 2 using reverse temperature and logarithmic time for leaching 40% and 60% Fe in Fig. 1. The fact that two straight lines obtained being parallel each other means that the mechanism keeps unchanged at different leaching stage. Apparent activation energy of 68.9 kJ/mol, which indicates the process is under surface chemical reaction control, is obtained as the product of the straight lines' slope and ideal gassing constant.

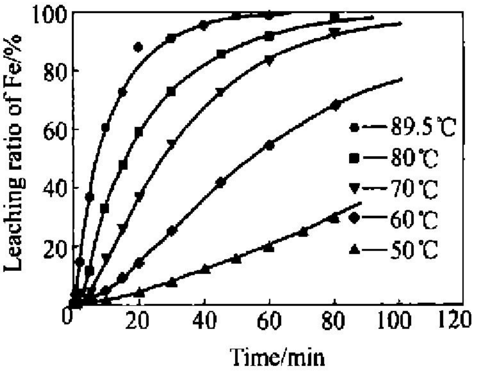

Fig. 1 Effect of temperature on leaching of non-activated pyrite
($[HNO_3] = 1.5$ mol/L; $[H_2SO_4] = 1.5$ mol/L)

Figs. 3 − 5 are the kinetic curves for leaching of pyrite activated for 10 min, 20 min and 40 min respectively. It seems that active sites may occupy

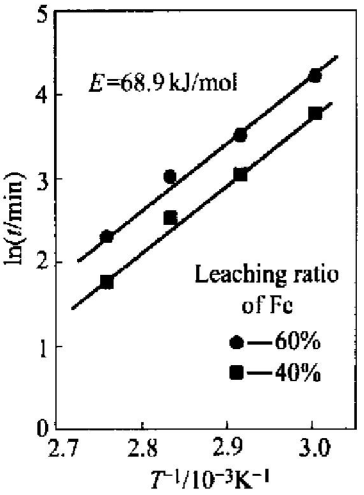

Fig. 2 Arrhenius plot for leaching of non-activated pyrite

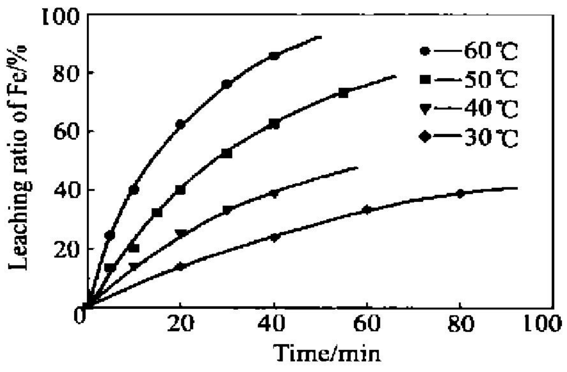

Fig. 3 Effect of temperature on leaching of pyrite activated for 10 min
($[HNO_3] = 0.5$ mol/L; $[H_2SO_4] = 1.5$ mol/L)

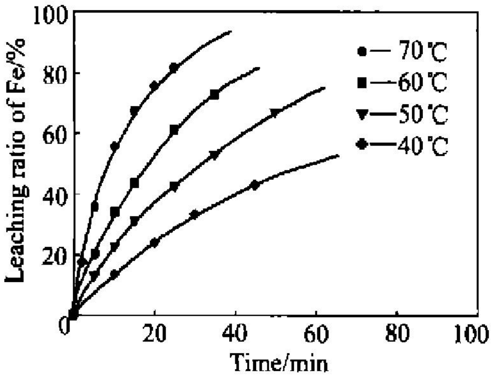

Fig. 4 Effect of temperature on leaching of pyrite activated for 20 min
($[HNO_3] = 0.5$ mol/L; $[H_2SO_4] = 1.5$ mol/L)

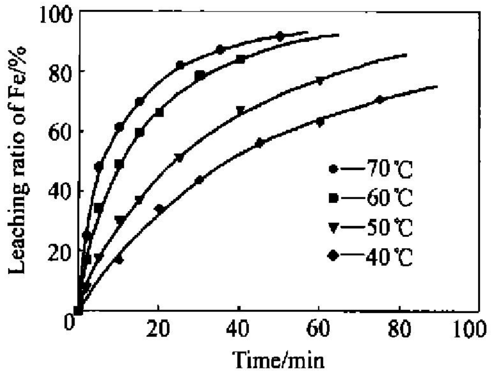

Fig. 5 Effect of temperature on leaching of pyrite activated for 40 min
($[HNO_3] = 0.5$ mol/L; $[H_2SO_4] = 1.5$ mol/L)

almost the whole surface area since induction time disappeared after MA. Apparently leaching is enhanced a great deal after MA of pyrite. One can found that the time need for leaching 40% Fe are compressed to about 30 min, 18 min and 16 min, in contrast with that for non-activated condition.

Increase of specific area, one of the results of milling for present case, is also beneficial for leaching. So it will be unilateral to discuss the activation effect only according to the phenomenon of speeding up in leaching. Apparent activation energy, a kinetic parameter which is independent of surface area of solid reactant and concentration of liquid reactant, should be reliable for discussing the effect of MA.

From the Arrhenius plots Figs. 6 − 8 corresponding to kinetic results in Figs. 3 − 5, the apparent activation energy for pyrite activated for 10 min, 20 min and 40 min is calculated to be 57.7 kJ/mol, 56.6 kJ/mol and 50.6 kJ/mol, respectively. According to the theory of MA, part of mechanical energy can be transformed into chemical one and stored inside solids in form of various imperfection. Thus its potential energy becomes higher than that of untreated one. Succeedingly, less energy (lowered apparent activation energy) is needed to get the energy level of middle active complex when taking part in chemical reaction. So the apparent activation energy tested becomes smaller with prolonging treating time, as shown in Fig. 9.

3.2 Mechanical activation of molybdenite

Fig. 10 shows the kinetic curves for leaching of non-activated molybdenum at different temperatures. Like

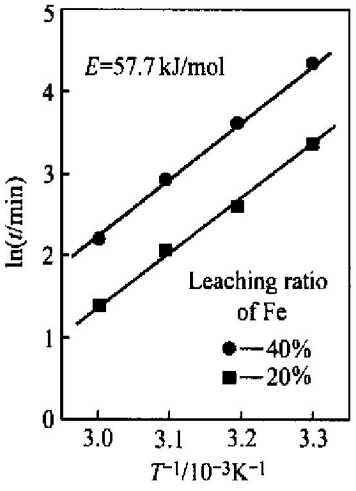

Fig. 6 Arrhenius plots for leaching of pyrite activated for 10 min

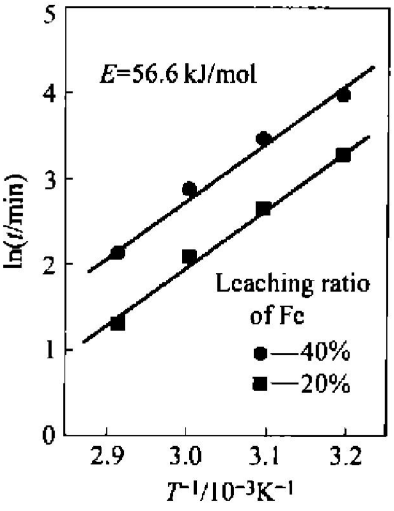

Fig. 7 Arrhenius plots for leaching of pyrite activated for 20 min

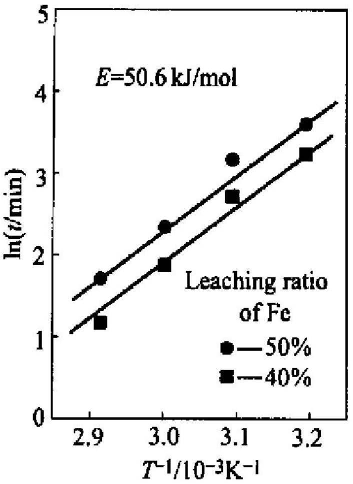

Fig. 8 Arrhenius plots for leaching of pyrite activated for 40 min

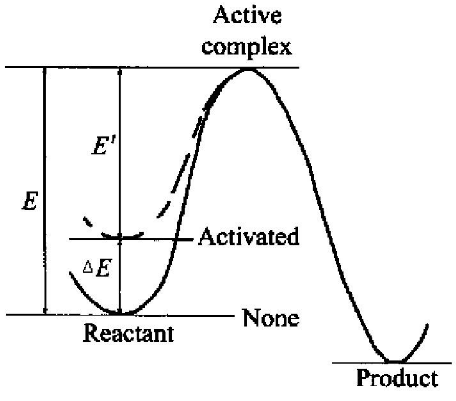

Fig. 9 Change of system inner energy with reaction coordinate

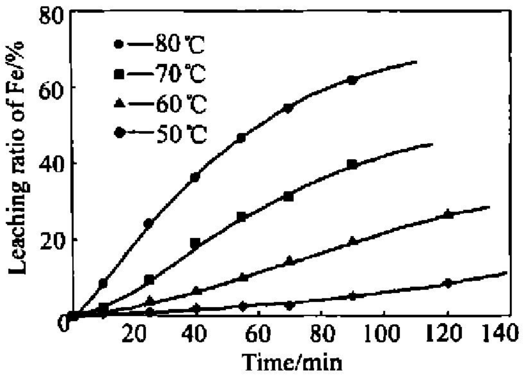

Fig. 10 Effect of temperature on leaching of non-activated molybdenite
([HNO_3] = 2.0 mol/L; [H_2SO_4] = 1.0 mol/L)

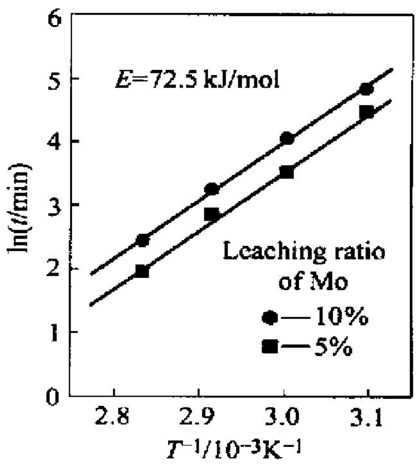

Fig. 11 Arrhenius plots for leaching of non-activated molybdenite

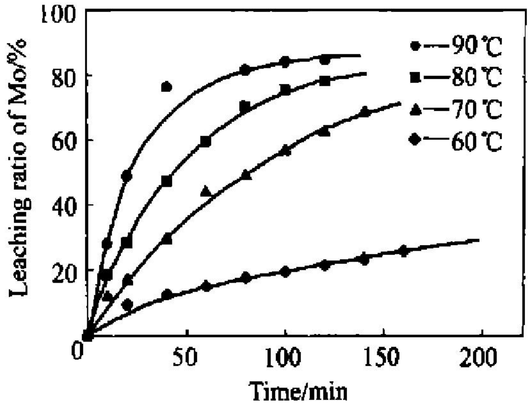

Fig. 12 Effect of temperature on leaching of molybdenite activated for 10 min
([HNO_3] = 1.2 mol/L; [H_2SO_4] = 1.5 mol/L)

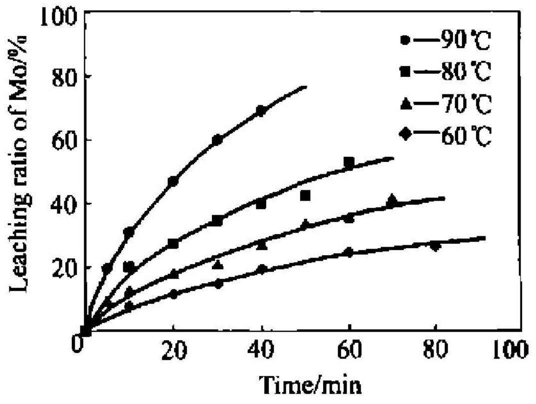

Fig. 13 Effect of temperature on leaching of molybdenite activated for 20 min
([HNO_3] = 1.2 mol/L; [H_2SO_4] = 1.5 mol/L)

pyrite, there exists induction time that effected by temperature. The apparent activation energy obtained from Fig. 11 is 72.5 kJ/mol. This value is an indication that the process is under chemical reaction control.

The kinetic curves and corresponding Arrhenius plots for leaching of molybdenite activated for 10 min, 20 min and 40 min are shown as Figs. 12 ~ 14 and Figs. 15 ~ 17, respectively. The calculated apparent activation energy decreases in series of 69.7, 68.7 and 66.5 kJ/mol with prolonged retreating time.

3.3 Crystal structure and its effect on activation

Molybdenite appears to be inert towards MA since 40 min pretreatment can only made the apparent activation energy be 6.0 kJ/mol lower than that of untreated one(as shown in Fig. 18). But for pyrite, this value is 18.3 kJ/mol. The lattice energy

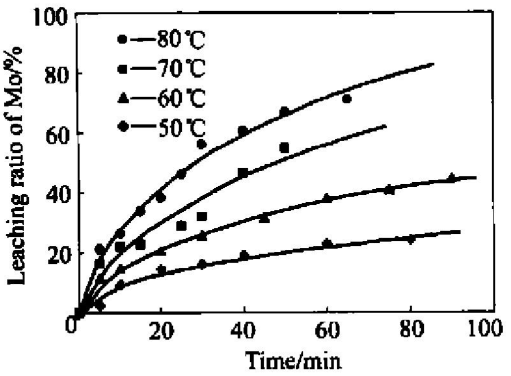

Fig. 14 Effect of temperature on leaching of molybdenite activated for 40 min

([HNO$_3$] = 1.2 mol/L; [H$_2$SO$_4$] = 1.5 mol/L)

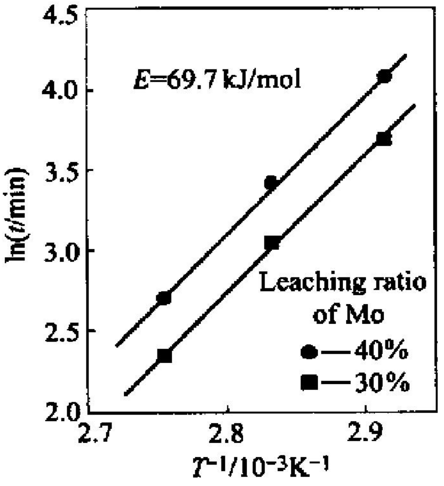

Fig. 15 Arrhenius plots for leaching of molybdenite activated for 10 min

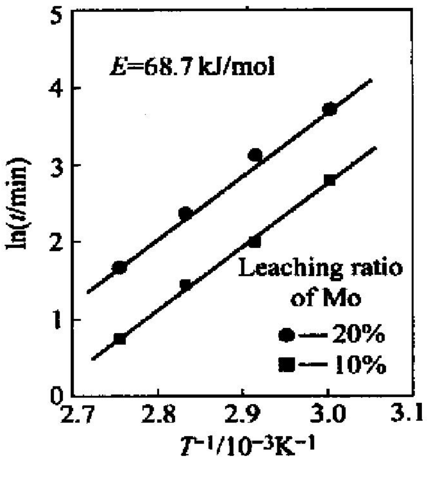

Fig. 16 Arrhenius plots for leaching of molybdenite activated for 20 min

of pyrite and molybdenite are 856 kJ/mol and 803 kJ/mol, respectively[23]. It seems abnormal that according to Criado's result, the changes in apparent activation energy should be grossly same.

To understand such “abnormal” phenomenon, review of the structure of two minerals is necessary. The structure of pyrite is illustrate in Fig. 19[24]. Pyrite has a space group symmetry of Pa3. It possesses a rocksalt type structure, with the Fe^{2+} cations at the face-centers of the cubic cell and S$_2^{2-}$ dimers at the anion positions[25]. The S—S bond axes are aligned along the ⟨111⟩ directions. Each Fe atom is coordinated to six neighbouring S$_2$ dimers, with one S at each of the vertices of a distorted octahedron, while each S atom is coordinated to three Fe atoms and one S atom in a tetrahedral configuration. Cleavage is very indistinct and the hardness is 6-6.5.

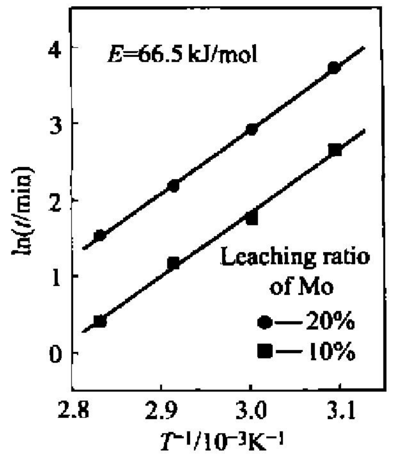

Fig. 17 Arrhenius plot for leaching of molybdenite activated for 40 min

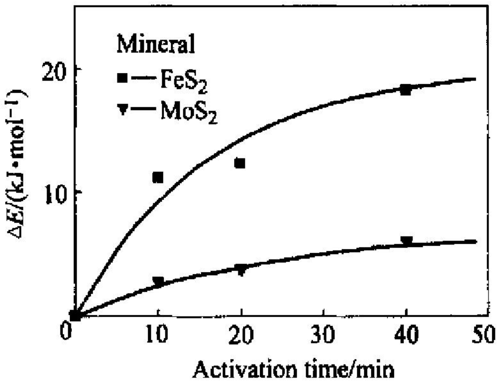

Fig. 18 Comparison of activation effects

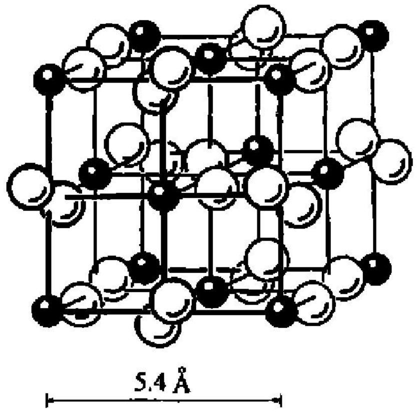

Fig. 19 Crystal structure of pyrite

Molybdenite's structure[24] is composed of molybdenum ions sandwiched between layers of sulfur ions, as shown in Fig. 20. There are two known poly-types of MoS$_2$ [26]: two-layer hexagonal and three-layer rhombohe-

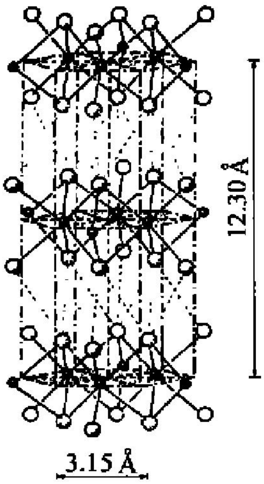

Fig. 20 Crystal structure of molybdenite

dral termed 2H and 3R, respectively. Both have regular layered structures with six-fold trigonal prismatic coordination of the Mo atoms by the sulfur atoms within the layers. 2H-MoS_2 has two layers per unit cell stacked in the hexagonal symmetry and belongs to the space group D_{6h}^4, while 3R-MoS_2 has three layers in the *c*-direction but has rhombohedral symmetry and belongs to the space group C_{3v}^5. The sulfur's layers are strongly bonded to the molybdenum, but are not strongly bonded(weak van der Waals forces) to other sulfur layers, hence its cleavage is perfect in direction in parallel with {0001}, forming thin sheets. The hardness is 1.

It is considered that the difference in crystal structure bring about the difference in MA effect. Molybdenite, being highly anisotropic, may counteract mechanical action through S—S inter layer slippage. After such slippage, molybdenite may transform from 2H to 3R or even inter-growth of the two. But its physical and chemical character keeps unchanged since the bonds between sulfur layer are almost still the same. (Such native trait enable us to use it as excellent lubricant for machining, aviation and missile. Its friction coefficient is less than that of ice). So it is plausible to consider that the increase in inner energy of molybdenite should be very small. According to Fig. 9, apparent activation energy should also change only a little. In other words, molybdenite is inert towards MA.

Compared with molybdenite, pyrite is isotropic and lack of cleavage. Intense mechanical action can only lead to breakage of chemical bond, causing crack of crystal or bring imperfection. Crack is not considered here though it gives new surface and simultaneously increases surface energy. Accumulation of various imperfection produced made the atoms in parts or whole of pyrite crystal depart from its original chemically stable state. Thus mechanical energy is transferred into imperfection energy and stored. So pyrite is sensitive to MA.

In fact, this conclusion do not conflict with that of Criado. For convenience, the data of Criado are listed in Table 3 and Table 4. The structure and cleavage data listed in Table 4 are from Refs. [24, 27, 28].

Table 3 Apparent activation energy for thermal decomposition of alkaline earth carbonate

Activation time/ h	$\Delta E/(\mathrm{kJ\cdot mol^{-1}})$			
	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
0	121	163	251	259
0.5	100		205	
2.0				188
3.0	100			
4.0				176
4.5		163		
6.0			172	
8.0		155	167	
10.0	105			
12.0		138		
24.0	105	134		

Table 4 Characterization of alkaline earth carbonate

Substance	Lattice energy/ $(\mathrm{kJ\cdot mol^{-1}})$	Group type	Cleavage
$MgCO_3$	3180	Calcite	[1011], perfect
$CaCO_3$	2987	Calcite	[1011], perfect
$SrCO_3$	2720	Aragonite	[010], imperfect
$BaCO_3$	2615	Aragonite	[010], imperfect

As shown in Table 3, MA of $MgCO_3$, $CaCO_3$, $SrCO_3$ and $BaCO_3$ leads to a diminution of the apparent activation energy of the thermal decomposition reaction. This becomes greater as the relative molecular mass of the salt increases. Carido considered that as the relative molecular mass of the salt increases, and their lattice energy listed in Table 4 decreases, the displacement of ions from their equilibrium lattice positions become easier. Consequently, there is an increase in the stored deformation energy induced by the grinding process in the order of $MgCO_3$, $CaCO_3$, $SrCO_3$ and $BaCO_3$. This appears to be a sound explanation.

But our analysis of the data in Table 3 disclosed that, in fact, the activation effect of $MgCO_3$ and $CaCO_3$ is indistinct compared with that of $SrCO_3$ and $BaCO_3$. For instance, the changes in apparent activation energy for the decomposition reaction of the former two are 16 kJ/mol and 29 kJ/mol, respectively. But those values are up to 84 kJ/mol for the later two activated for only 8 h and 4 h. According to Carido's explanation, there should be a sudden decrease of lattice energy between $CaCO_3$ and $SrCO_3$, but in fact it changes smoothly.

Table 4 indicates that the former and later two are of different crystal structure. $MgCO_3$ and $CaCO_3$ belong to calcite type and show rhombohedral structure, having a space group symmetry of $R\bar{3}$. They show strong anisotropy since they exhibit perfect cleavage in direction parallel to [1011]. But $SrCO_3$ and $BaCO_3$ are of aragonite type and exhibit orthorhombic lattices, belonging to the space group of Pmcn. They behave more isotropy as they give only imperfect cleavage along [010]. So from our point of view, $SrCO_3$ and $BaCO_3$ should be more sensitive towards MA than $MgCO_3$ and $CaCO_3$. The reason Carido can justify himself in his discussion, though he neglected the effect of crystal structure, may lies in that such trend of changing caused by crystal structure is the same as that by lattice energy.

The present work arrived in only qualitatively that crystal structure affects MA more than lattice energy. Considering the complexity in crystal structure and composition, further accumulation and analysis of experimental data is necessary for forecast MA result quantitatively or semi-quantitatively.

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