ASM INTERNATIONAL
Metals Park, Ohio 44073

PROCESSING OF MECHANICALLY ALLOYED AMORPHOUS $Co_{85}Zr_{15}$

Hiroshi Kimura
Department of Mechanical Engineering
National Defense Academy
Yokosuka 239, Japan

Masayoshi Kimura
Graduate school
National Defense Academy

Takao Ban
On leave from Mitui Miike Engineering Co., Ltd.
Tochigi Branch, Tochigi 328-03, Japan

Rapidly Solidified Materials: Properties and Processing
Proceedings of the 2nd International Conference on
Rapidly Solidified Materials
San Diego, California, 7-9 March 1988

Published by ASM INTERNATIONAL

8802-004

SAN: 204-7586

8802-004

PROCESSING OF MECHANICALLY ALLOYED AMORPHOUS $Co_{85}Zr_{15}$

Hiroshi Kimura
Department of Mechanical Engineering
National Defense Academy
Yokosuka 239, Japan

Masayoshi Kimura
Graduate school
National Defense Academy

Takao Ban
On leave from Mitui Miike Engineering Co., Ltd.
Tochigi Branch, Tochigi 328-03, Japan

The mechanical alloying of elemental crystalline powders of Co and Zr was performed using a high energy rotating-arm ball mill with 300 rpm and various flow rates of cooling water, in order to make a diagram of a time-temperature transformation of a solid state amorphization. The flow rate can vary the attrition temperature,Tp, at a plateau occuring prior to the onset of an exothermal reaction from 65 to 95 ℃. This Tp's increase leads to a reduction in the attrition period needed to complete the solid state amorphization of $Co_{85}Zr_{15}$ from 8 to 14 hr. The periods(t) at the onset and the completion of amorphization,as defined by an Avrami-Johnson-Mehl plotting are expressed by an Arrhenius equation of $1/t=A\exp(-H/kT)$ where A and k are the usual meanings. We obtain the activation energy(H) for an amorphizing transformation betweeen 1.6 and 1.76 eV at an early stage and a late stage of the solid state reaction which are definitely devided by two Avrami exponents of 1.6 and 2.9.

1. INTRODUCTION

RECENTLY,it has been shown that a grinding of elemental crystalline powders makes it possible to get a solid state amorphized phase of the blend composition[1]. It becomes to be recognized that a mechanical alloying processing using a high energy rotating-arm ball mill is namely a promissing technique to the material development from which to realize the mass prodution,near ambient temperature,of a variety of amorphous metallic powders of widespread applications[2]. At the same time,the micromechanism involved in a solid state amorphization by mechanical alloying has been the subject of considerable controversy. It has been suggested that ball milling consists of some complex processes,including a collision,a wearing,a shearing,an intense cold welding and so on. These are conditions which make the measurement and definition of process variables of solid state amorphizations difficult.

In order to answer the demands placed by the requirments of the foregoing,we have developed a high energy rotating-arm ball mill for a solid state amorphizing transformation that has a large grinding capacity and fringe equipment to measure process parameters of the attrition temperature and the torque[3]. One of the authors have previously arrived at an Avrami-Johnson-Mehl equation of a solid state amorphization by mechanical alloying,in which,using 300 rpm,two Avrami exponents of 1.5 and 2.9 are derived at a early stage and late stage of a solid state reaction respectively[4]. In order to establish a mechanical alloying processing for a solid state amorphizing transformation,we further have to know how process variables of the attrition temperature and the torque applied to powders optimize the rate of a solid state amorphization.

Here,we report the mechanical alloying of elemental crystalline powders of Co and Zr at various flow rates of water cooling of an attrition atmosphere inside the tank,in order to make a diagram of a time-temperature transformation of a solid state amorphization of $Co_{85}Zr_{15}$ by mechanical alloying.

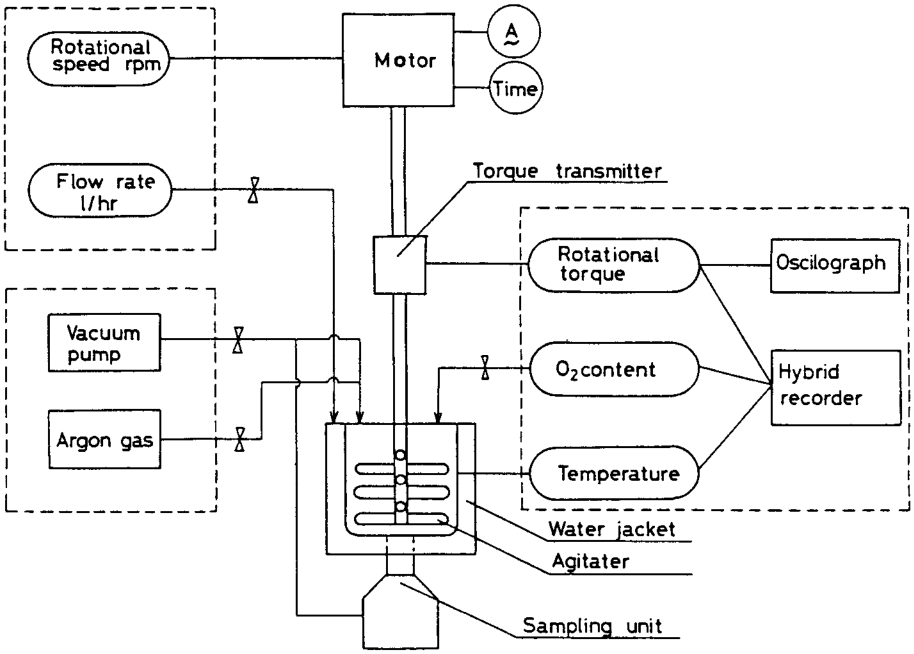

Fig.1 Schematic system of the high energy rotating-arm ball mill used in this study.

2. EXPERIMENTAL PROCEDURE

Elemental crystalline powder mixture Co$_{85}$Zr$_{15}$ was mechanically alloyed under an Ar atmosphere using a recently developed high energy ball mill[3] in a range of a flow rate of cooling water(Cw) from 50 to 1200 ℓ/hour in the case of angular velocity of 300 rpm. A solid state amorphizing transformation of Co$_{85}$Zr$_{15}$ was monitored by the attrition temperature inside the tank and the torque;these process variables can be measured through fringe equipments as illustrated in Fig.1. X-ray diffraction was used to characterize the structure of mechanically alloyed powders against milling time.

3. RESULTS AND DISCUSSION

3.1 MECHANICAL ALLOYING PROCESS AT VARIOUS COOLING WATER FLOW RATES-Fig.2 shows the attrition temperature against milling period with the flow rate of cooling water ranging from 50-1200 ℓ/h in the case of 300 rpm,for mechnaical alloying of crystalline powders of Co and Zr. For all of agitation tested here, we can see the occurance of the plateau in the curve of milling time dependence of the attrition temperature,following a sharp rise. The onset of an exothermal reaction can be defined by a rise of attrition temperature from the level of the plateau. It is found that the milling period necessary to com-

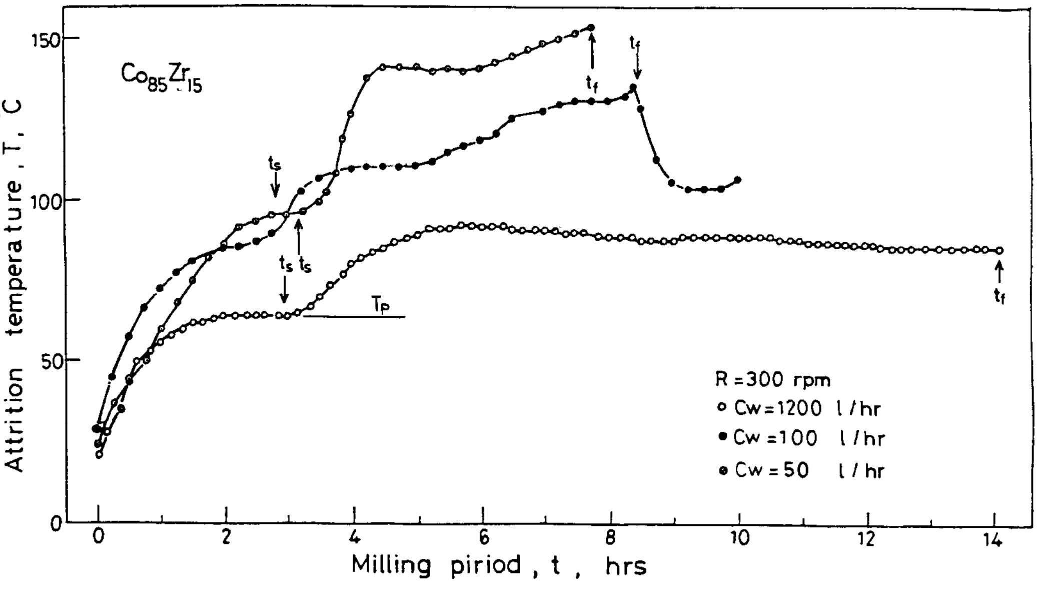

Fig.2 Attrition temperature versus milling time at various flow rates of cooling water in a range of 50-1200 ℓ/h for mechanical alloying of elemental crystalline powder mixture Co$_{85}$Zr$_{15}$.

plete a solid state reaction,tf,as determined from a sudden drop of the torque[4],greatly increases from 8 to 14hrs,if the cooling water is increased from 50-1200 ℓ/hr.

Fig.3 shows X-ray diffraction patterns of mechanically alloyed $Co_{85}Zr_{15}$ for 1h20min,4h50 min,8h30min and 11h50min in case of Cw=100 ℓ/h. There were only crystalline peaks at the region of the plateau(1h20min) where a formation of multi-layers proceedes,indicating no amorphization. At the first exothermal peak of the solid state reaction of $Co_{85}Zr_{15}$(4h50min),the X-ray diffraction pattern consisted of amorphous broad peak and remaining Co peak,showing a solid state amorphizing transformation at the interfaces of multilayers. Further,one can see only amorphous broad peak without any crystalline peaks at the completion of solid state reaction(8h30min). The intensity and position of amorphous broad maximum do not change after a droping of attrition temperature(11h50min). Note that the flow rate of cooling water has a strong effect on the mechanical alloying period at the completion of the solid state amorphization of elemental crystalline powder mixture $Co_{85}Zr_{15}$.

3.2. EFFECTS OF WATER FLOW RATE ON MUTILAYER FORMATION-Fig.4 shows the attrition temperature at plateau,Tp,against flow rate of cooling water. With the water flow rate is increased in a range from 50-1200 ℓ/h, the Tp decreases from 95-65℃. With this result,we can simply say that the occurence of the plateau is resulted from a stable proceeding of the multilayer formation without an exothermal reaction and an extra applied torque,and then its level,Tp,can be determined by the balance between an exotherm inferred from an agitating ball charge at a constant rotational speed and a cooling by water flow. In other words,we can select a reaction temperature,Tp,at will by varying the water flow rate, in order to control an rate of a solid state amorphizing transfomation.

Fig.5 shows the milling time at a rise of attrition temperature from Tp,defined as the onset time of an exothermal reaction,t_S,as a function of flow rate. We see that the t_S decreases as the water flow rate is increased from 50-1200 ℓ/h, this behavior is contrary to an increase in t_f as shown in Fig.1. A rising of attrition temperature leads to a higher consolidation rate which is conducive to a larger particle size[5] and consequently could delay the t_S. So,the defined onset time implies the milling time required to get a critical layer thickness for the onset of a solid state reaction,not an incubation period of a solid state amorphization.

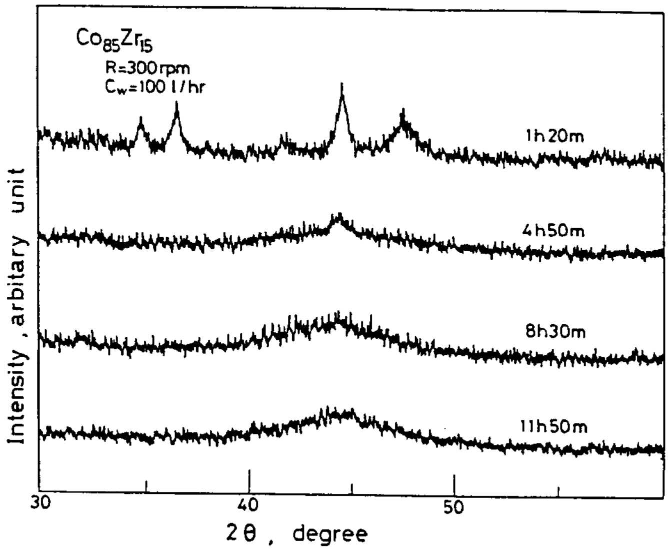

Fig.3 X-ray diffraction traces of mechanically alloyed $Co_{85}Zr_{15}$. Measurements taken at milling time of 1h20min,4h50min,8h30min and 11h50min.

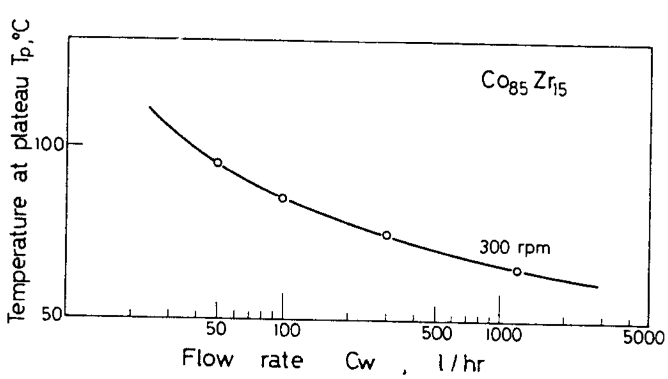

Fig.4 Plateau attrition temperature as a function of flow rate of cooling water for mechanically alloyed $Co_{85}Zr_{15}$.

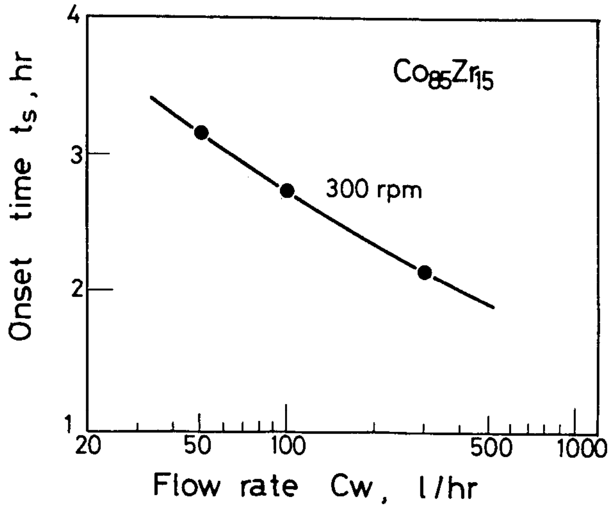

Fig.5 Onset time versus logarithmic flow rate for mechanical alloying of $Co_{85}Zr_{15}$.

3.3. EFFECTS OF TEMPERATURE ON A SOLID STATE AMORPHIZATION-Fig.6 shows a formation enthalpy of an amorphization, as derived from an exothermal reaction(;see ref.4 for a detail description of the deviation procedure) as a function of the flow rate of the cooling water. We see a constancy of the formation enthalpy against the plateau temperature, Tp, in case of 300 rpm. The Tp at 1200 ℓ/h seems to deviate somewhat from the constancy; this deviation may be attributed to a lack of a drop of the attrition temperature to the level of Tp at the late stage of a solid state amorphization through a heat transfer from agitating balls with a higher temperature relative to the atmosphere temperature inside the tank. The critical multilayer thickness and the torque may have an effect on the amorphization enthalpy. The constancy of Fig.6 may validate that these attrition tests were performed under the same conditions of the critical layer thickness and the torque applied to powders.

Under the circumstances stated above, let us make an Avrami-Johnson-Mehl analysis for temperature's dependences of reaction rates of solid state amorphizing transformations. For amorphizations at three temperatures of 65,85 and 95℃ of Fig.2, Fig.7 are logarithmical plots of the amorphized volume, x, versus the logarithmic of the milling time, t, from the onset time based on the following relationship:

$$x = 1 - \exp(\alpha t)^{n} \qquad (1)$$

where n is an exponent and α is a kinetic constant. The value of n is dependent on the nucleation and growth mechanism of an amorphizatin.

In the plotting of Fig.7, we see two linear portion of the curves at the early stage and the late stage of solid state amorphizations in an good agreement of the previous result by Kimura[4]. For solid state amorphizations at various temperatures, the first stage is linear with $1.6<n<1.7$, indicating a diffusion controlled transformation, and the second stage has Avrami exponent $2.8<n<3.0$, suggesting a interfaced controlled celluar transformation.

The position of the amorphous peak shifts to a larger scattering angle during the first stage of the amorphization as shown in Fig.3, although this position does not change during the second stage[4]. The former event shows a composition change of an amorphized phase during milling, but the latter event indicates almost the same composition. These findings give support to the idea that an amorphization by mechanical alloying occurs by two simple processes of a nucleation and growth mechanism. We here consider a possiblity of that the appearance of the second stage is a deviation from the first linear

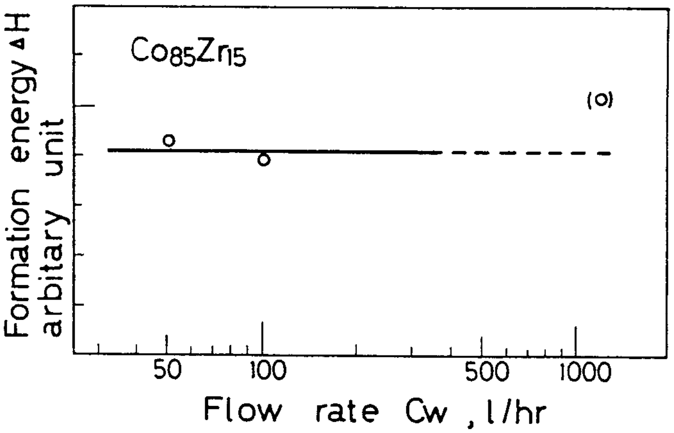

Fig.6 Relationship between formation enthalpy of an amorphization of $Co_{85}Zr_{15}$ and flow rate.

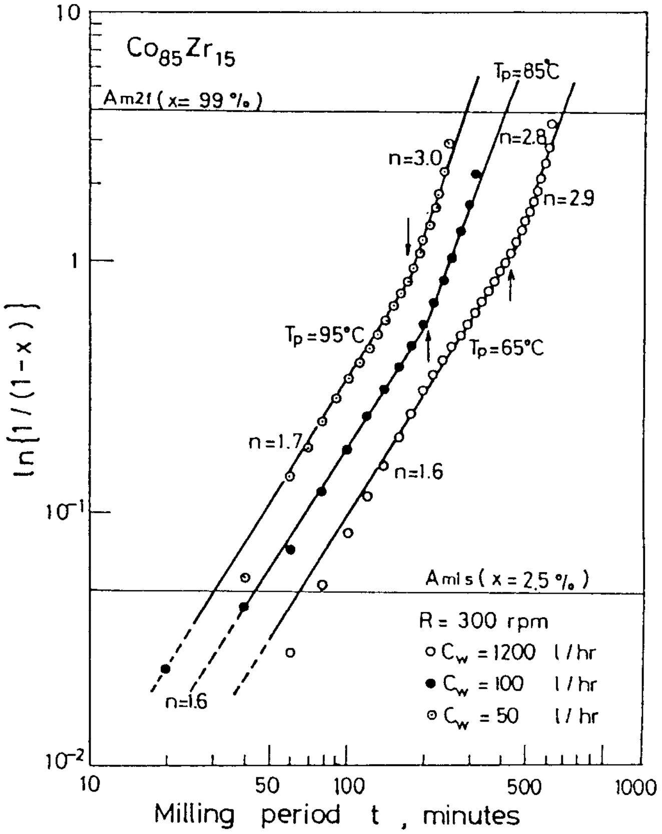

Fig.7 Avrami-Johnson-Mehl plot of solid state amorphized $Co_{85}Zr_{15}$ volumes at various plateau attrition temperature.

portion, if a reduction of a thickness of the multilayer occurs during further milling. However, the powders size remains almost constant or increases after the onset of an amorphization[4,6], and thus it is difficult to get a further reduction of the multilayer thickness.

Next, deduce an activation energy for a solid state amorphizing transformation(H) of Co_{85}-Zr_{15}. Fig.8 is Arrhenius plots of the milling times(t) necessary to get amorphized volumes of x=2.5,45 and 80%. It can be seen that the plot of the reciprocal milling time versus the reciprocal temperature shows good linearity and that the data can therefore be represented by

$$1/t = A\exp(-H/kT) \qquad (2)$$

where k is the Boltzman constant, and A is preexponential factor. The activation energy, $1.6<H<1.76$ eV is obtained for the first and second stages of the amorphization of $Co_{85}Zr_{15}$ by high energy ball milling with 300 rpm. The activation energy will be an important material parameter for the discussion of the mechanism of a solid state amorphization.

Furthermore, we describe the diagram of a time-temperature-transformation(TTT diagram) of the amorphization of $Co_{85}Zr_{15}$ by mechanical alloying. Fig.9 shows the milling time at x=2.5%, defined as the onset of the first amorphization (Am_{1S}), the time at the transition between the first stage and the second stage(Am_{1f} or Am_{2S}) and the time at x=99%, defined as the completion of the amorphization (Am_{2f}) for various temperatures. The reaction temperature of the amorphization of $Co_{85}Zr_{15}$ by mechanical alloying is considerably lower, comparing to an isothermal solid state reaction of sputtered multi-layers around 200℃[7]. The mechanical alloying time at the completion of the amorphization is much shorter than that of a solid state amorphizing transformation of sputtered multi-layers. The amorphization by mechanical alloying occurs at the interfaces of muti-layers assisted by a considerable higher shear stress. So, the applied shear stress could promote a solid state amorphizing transformation at a relative lower temperature, which is a thermal activated process.

4. CONCLUSIONS

The mechanical alloying of elemental crystalline powders of Co and Zr using the flow rates of cooling water in a range of 50-1200 ℓ/h was studied by monitoring mainly the attrition temperature as a function of milling time. The decrease in flow rate leads to the increase in the attrition temperature, Tp, at the plateau occuring against the attrition time from 65-95℃.

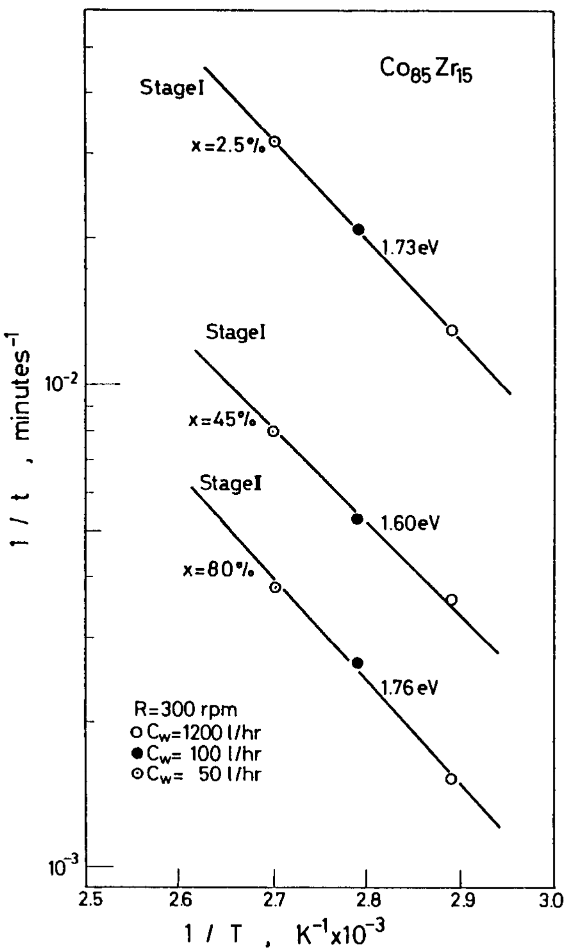

Fig.8 Arrhenius plots of milling times at volume x=2.5,45 and 80% for amorphized $Co_{85}Zr_{15}$ volume.

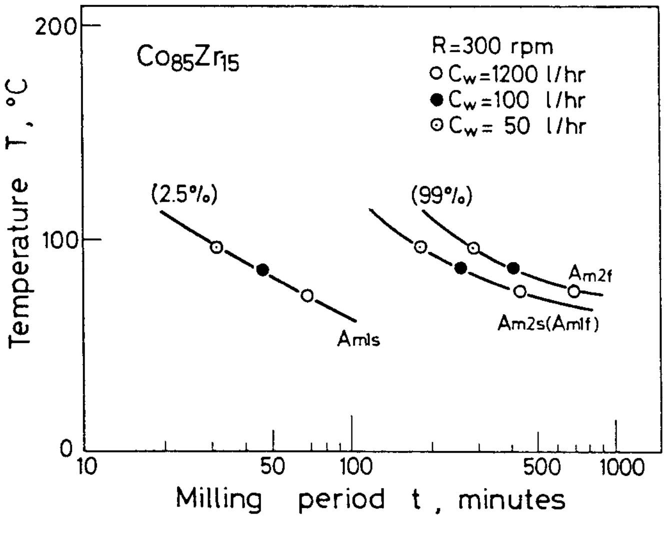

Fig.9 Diagram of time-temperature-transformation of solid state amorphizations of $Co_{85}Zr_{15}$ by mechanical alloying.

This Tp's increase causes a reduction in the milling period at the completion of a solid state amorphization of $Co_{85}Zr_{15}$. The attrition periods(t) at the onset and the completion of a solid state amorphization are expressed by an Arrhenius equation, $1/t=A\exp(-H/kT)$. The activation energy for solid state amorphizing transformations by mechanical alloying $1.6<H<1.76$ eV is obtained at the first and second stages of the exothermal reaction of $Co_{85}Zr_{15}$ where two Avrami exponents of 1.6 and 2.9 were derived respectively.

REFERENCES

1. R.B.Schwarz,R.R.Petrich and C.K.Saw, J.Non-Crystalline Solids,76,281(1985).
2. H.Kimura and T.Ishizaki,Proc.11th Symposium of Composite Materials in Japan,Japan Society for Composite Materials,42(1986).
3. H.Kimura,M.Kimura and F.Takada,Conf.on Solid State Amorphizing Transformations,(Los Alamos 1987). J.Less-Common Metals in the press.
4. H.Kimura,Sintering'87,(Tokyo,1987 Nov.) in the press.
5. H.Kimura and M.Kimura,to be published.
6. H.Kimura and F.Takada,Mater.Sci.Engng. in the press.
7. K.Samwer,A.Regenbrecht and H.Schöder,Rapidly Quenched Metals,eds.S.Steeb and H.Warlimont, Elesevier Science Publishers B.V.,1577(1985).