Study on Liquid Metal Embrittlement of Carbon Steels (Report 1)†

— Penetration Behavior of Liquid Metal —

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Abstract

The effect of penetration of liquid metal on the flow stress and fracture properties of LME of carbon steels by Cd-5Zn, Cd-50Zn and pure Cd has been studided. Using smooth and notched speciments, experiments were conducted just abobe the melting points of the emrittlers, at 350°C, and crosshead rate in a tensile test was 5mm/min.

It is shown that apart from the reduction in ductility the stress-strain curves are slightly altered due to the grain boundary penetration of liquid metals. The results of tensile test with notched specimen also indicate that for the occurrence of LME, the stress or load has to exceed a critical value. Moreover, the mean penetration length at fracture could be estimated, assuming that the fracture stress of steel with liquid metal equals the ultimate stress (i.e. actual stress) without liquid metal. The data suggest that such LME is evaluated by the mean penetration length.

KEY WORDS: (Liquid Metal Embrittlement) (Carbon Steel) (Zinc) (Penetration)

1. Introduction

Embrittlement of solid metals under applied internal tensile stress when wetted with an appropriate liquid metal is usually known as liquid metal embrittlement, LME[1) 2) 3)]. However, although about such a phenomenon many invenstigators[4)] have so far reported, their experiments are always accompanied with some experimental difficulties as follows: 1) technique on direct observation 2) LME testing under the high temperature conditions of solid/liquid couples in question, 3) a lack of the most desirable method of testing and 4) requirement of reliable wettability. Thus, for the lack of a systematic study no model which explains clearly about the occurrence and the severity of LME, seems to have developed. Some studies which were reported with respect to the occurrence or the selectibity of LME, are also contradictory, as described below. For instance, zinc/steel couple which is technically important is encountered in hot dip galvanizing of large welded structures or the welding of coated steel. Genders[5)] and Watanabe[6)] have observed that zinc is almost immune to LME of steel, but Tanaka et al.[7)] and Kikuchi[8)] have reported that such steel is markedly embrittled by zinc. In the same type of study, Radeker [9)] also observed embrittlement of a steel, using binary liquid Cd-Zn alloys. The question of whether zinc increases the embrittlement of steel or not is a typical example of much of the confusion and contradiction to be found in the literature on LME. Moreover the penetration behavior and the evaluation of LME remain unknown and no accurate method of predicting failures is yet available. Whereas about penetration behavior of liquid metals a few works have been conducted on non-ferrous materrial, there has been no study.

The present work was undertaken to clarify the behavior of penetration by a liquid metal and to evaluate the susceptibility of carbon steel to LME. The studies were carried out on Armco iron and on a variety of carbon steels, using Cd-Zn alloys as a liquid metal. Because a Cd-Zn system is a binary eutectic alloy it can be expected to lower the testing temperature.

2. Experimental Procedures

2.1 Materials and Specimens

Five base metals utilized are Armco iron, SS34, SS41, S25C and S45C with a varying carbon content. The chemical compositions of steels used in this study are given in **Table 1. Figure 1** shows the dimensions of the tensile test speciments for (a) smooth specimen (unnotched specimen) and (b) notched specimen. The specimens of both Armco iron and SS34 steel were machined from 16mm thickness sheet in the rolling direction and the others were done from 19mm diameter bar, respectively. After machining, these speciments were annealed at 600°C for one hour in

† Received on September 30, 1982

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Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka, Japan

Table 1 Chemical compositions of carbon steels (Wt %)

Materials	C	Si	Mn	P	S
Armco Iron	0.028	0.004	0.007	0.003	0.001
SS 34	0.066	0.030	0.290	0.015	0.014
SS 41	0.139	0.220	0.460	0.021	0.022
S 25 C	0.280	0.220	0.450	0.020	0.024
S 45 C	0.470	0.230	0.660	0.020	0.019

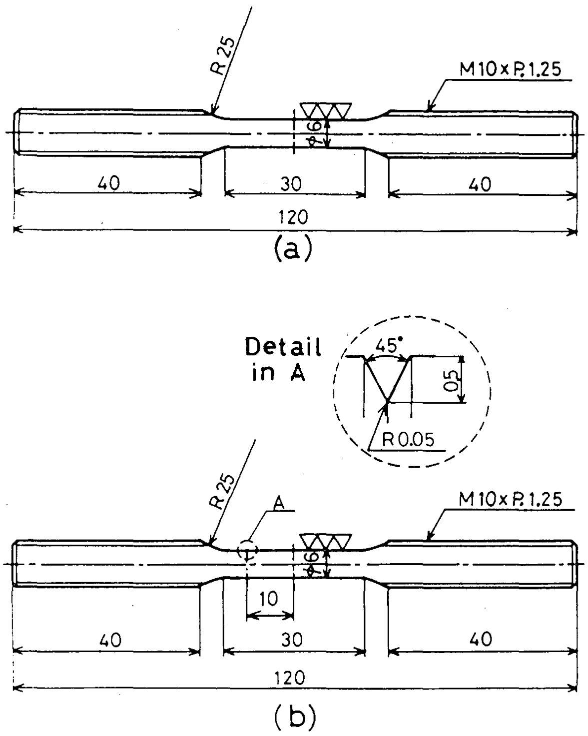

Fig. 1 Dimensions of tensile test speciments, (a) smooth specimen, (b) notched specimen

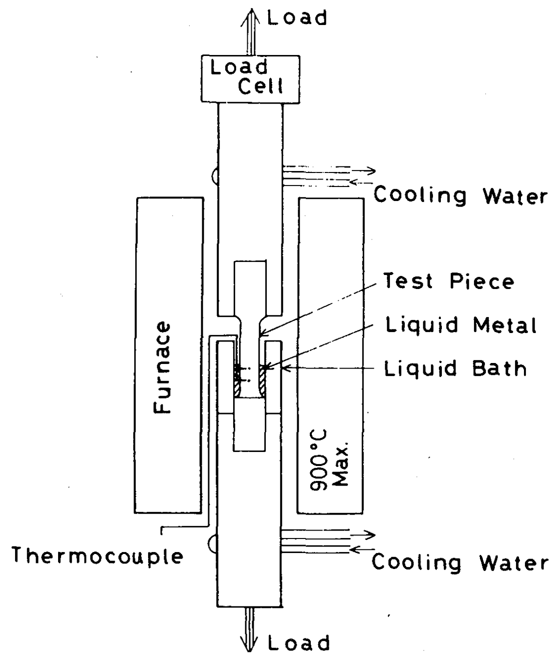

Fig. 2 Diagramatic arrangement of testing apparatus used for LME

vacuum (about 10^{-3} Torr) to remove any residual stress. Before the tensile tests, the surface of the specimen was polished with emery paper (No. 800) and then cleaned and degreased in aceton using ultrasonic cleaner.

As liquid alloys, both Cd-5at.%Zn (M.P. about 310°C) and Cd-50at.%Zn (M.P. about 310°C) were made in electric furnace from pure Cd (99.9%) and Zn (99.9%).

Liquid alloy deposited on fracture surface was chemically removed with about 2% H_2SO_4 aqueous solution to observe clearly the fracture sunface by optical microscopy.

Flux used in this study is a powder of NH_4Cl-52mol% $ZnCl_2$.

2.2 Testing Apparatus

Tensile tests were performed by an Instron tensile machine (10 tons) using a crosshead speed of 5mm per minute. Diagramatic arrangement of the testing apparatus, specimen, liquid bath, furnace and thermocouples is shown in **Fig. 2**. In this study, the temperatures of a specimen were measured by thermocouples at two locations along the gage length. Steel-vessel was then screwed up the specimen and, to prevent the leakage of liquid metal, its bottom was sealed with alumina cement. then, fine globules of embrittling alloy (about 15grams) and flux were inserted into the vessel before tensile testing.

3. Results and Discussion

3.1 Preliminary Considerration of LME

In the first stage of this study, pure Cd, Zn, Cd-5Zn and Cd-50Zn alloys were spread-tested on steel tabs (50mm square x 0.8mm). Both Cd-5Zn and Cd-50Zn alloys, which have melting points of about 310°C, were the most desirable in spreading at lower temperature. And since the solubility of iron in liquid Cd is only $2x10^{-4}$wt.%[2] at 400°C, it may be identified as a more immune embrittler than zinc.

Figure 3 shows a comparison of the stress-strain curves in various environments (in air, in flux and in liquid metals). Macrophotographs of smooth 0.139% carbon steel fractured in various environments, as mentioned above, are also shown in **Fig. 4**. From these results, the stress-strain curve in flux is the same as the curve in air. In pure Cd, the flow curve of steel is shortened and a small change is noted in the ultimate

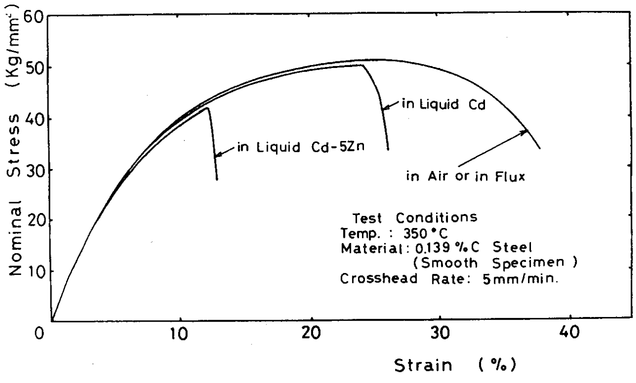

Fig. 3 Effect of LME on stress-strain diagrams

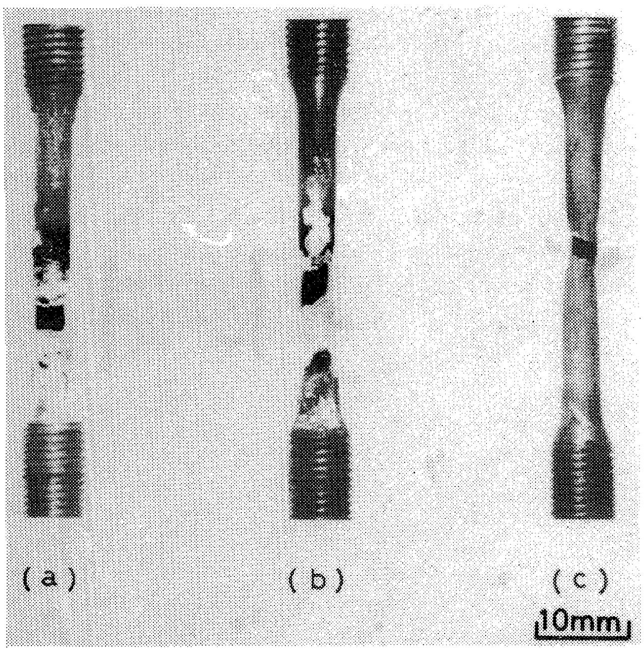

Fig. 4 LME photographs of Fig. 3, (a) left-Cd-5Zn liquid alloy, (b) middle-pure Cd, (c) right-without liquid metal

tensile strength. It is also shown that steel can be severely embrittled under tensile test by a small addition of Zn to pure Cd which slightly alters the flow curves of steel in comparison with the curve in air. However, the result was obtained only by carefully controlled experiments to distinguish the difference between the two curves, while Nicholas et al.[4] and Lynn et al.[13] have shown that such curves, are shortened but their shapes to fracture are not changed. Information regarding the mechanical aspect of LME is given below. With macrophotographs of steels fractured in various environments, the fracture in air or in flux was observed to be ductile with a local necking but that in liquid metals, as shown in Fig. 4, indicated a complicated and brittle appearance. On the tensile specimen in liquid Cd-5Zn alloy, the tendency was especially remarkable.

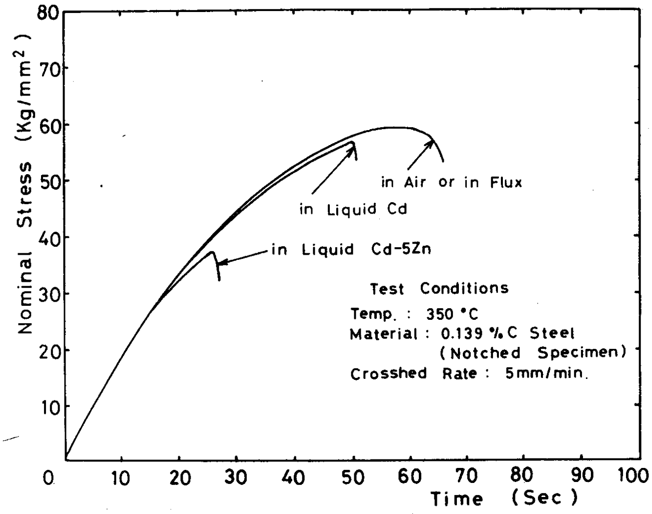

Fig. 5 Effect of LME on stress-time diagrams

However, in discussing the penetration behavior on LME, it is not easy to show how and to what degree the liquid metal penetrates into such a smooth specimen. So, it may be reasonable to expect that the penetration behavior can accurately be conducted using an appropriately notched specimen. Thus, the similar results using notched specimens in various environments are shown in **Fig. 5**. All of the specimens were fractured at the bottom of the notch, as expected above, and the propensity of LME was also the same as that of the smooth specimen.

From these results of the tensile tests, it is recognized that LME occures easily by a small addition of Zn to pure Cd and that a good study of penetration behaviour can be conducted using a notched specimen. Moreover, for the liquid Cd-Zn alloy/carbon steel couple used in this study, LME occurred with 100percent probability and then no scatter of the stress-strain curves was produced. It was therefore, considered that their couples can be effectively used to observe the penetration behavior of embrittlement for the various carbon steels.

3.2 Penetration Behavior by Liquid Metals

The effect of LME on the stress-time diagrams of the carbon steels (notched specimen) is shown in **Fig. 6**. From this figure, it is observed that the sensitivity of carbon steel with liquid metal (Cd-5Zn alloy) increases with increase of the carbon conent. A similar tendency is also observed in the tensile strength.

When the notched specimen was contacted with liquid metal, the flow curves (stress-time diagrams) of steels were also slightly altered as shown in Fig. 3 and 5. So, in order to clarify the cause, another tensile test was carried out in the following way: the crosshead was stopped at the appropriate loads prior to fracture and then the applied load was rapidly released and the specimen taken out of the furnace. **Figure 7** shows a typical photomicrograph of cross section cut longitudinally across the notch of the steel (0.066%C), when the crosshead was stopped 25 sec. after loading. It is observed microscopically that the intercrystalline penetration occurs prior to fracture. Since the fracture of steel in contact with liquid metal is invariably preceded by penetration of liquid metal, it is considered that such an edge effect may be a primary cotributor to the alteration of the flow curve.

In order to make clearer the nature of such penetration, authors adopted a maximum and mean penetraion lengths in this study. The illustration of the circumferential penetration at the bottom of the notch is shown in **Fig. 8**. Figure (a) shows a few aspects, in which a grain boundary penetration irregularly occurs. In order to assess the value of the mean area embrittled by grain boundary penetration, a modification is shown also in figure (a). So, we define Lpm as a maximum penetration length where the liquid metal reaches the inside of the substrate and $\bar{L}p$ as a mean penetration length. The maximum and mean lengths of grain boundary penetration by liquid Cd-5Zn alloy as a function of loading time are shown, for 0.28% and 0.47% carbon steel, respectively in **Fig. 9**. In both steels, the start time of penetration is about 10sec. after loading. In these cases, the process of penetration may be classified as follows: (1) first stage at which the pentration of liquid metal proceeds slowly: (2) second stage at which penetration is sudden and (3) third stage not related to LME. At the first stage of 0.47 and 0.28 carbon steels the loading time is less than 15sec. and 19sec. respectively. It is recognized that the start time of the second stage corresponds well with the start of the deviation on the flow curve as shown in Fig. 6. So, in order to clarify more this phenomenon, we stopped the crosshead at the first or second stage during the test. The results of the 0.47% carbon steel are shown in **Fig. 10.** Between $34kg/mm^2$ and $35kg/mm^2$ of nominal stress, there is a significant difference in LME progress. Namely the embrittlement of the 0.47% carbon steel occurred for a short time above the $35kg/mm^2$ stress, whereas at

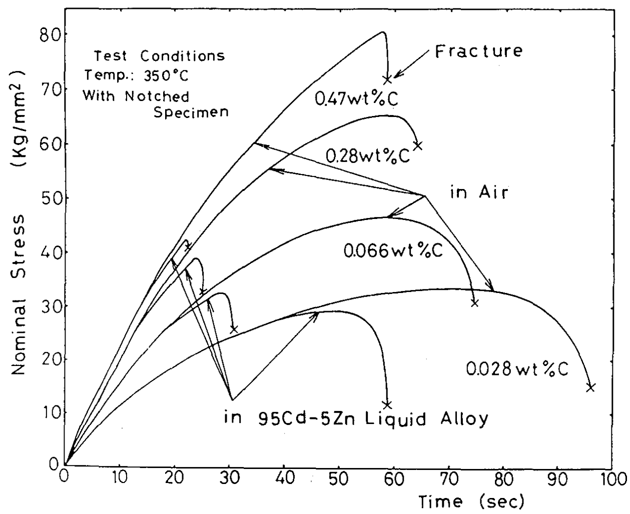

Fig. 6 Effect of LME on stress-time diagrams of various carbon steels

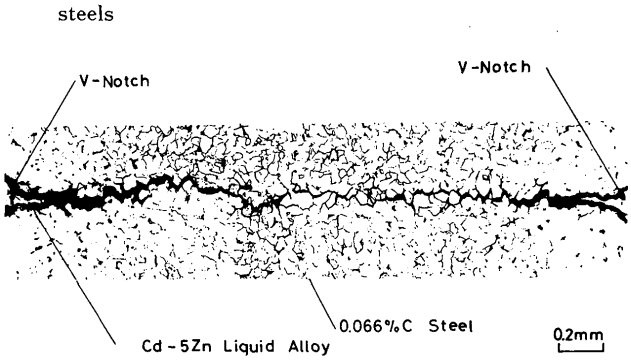

Fig. 7 Typical photomicrograph of grain boundary penetration of 0.066% carbon steel by liquid Cd-5Zn alloy

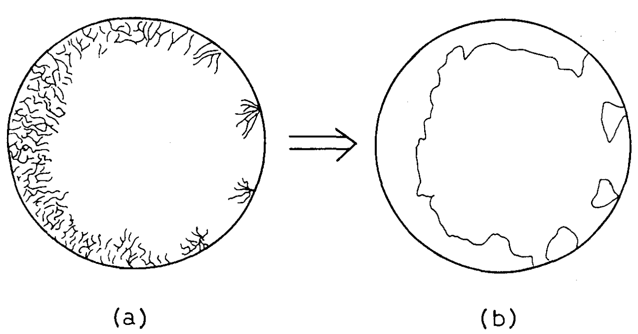

Fig. 8 Schematic views of penetration in bottom of notched specimen, (a) left-maximum penetration length,(b) right-mean penetration length

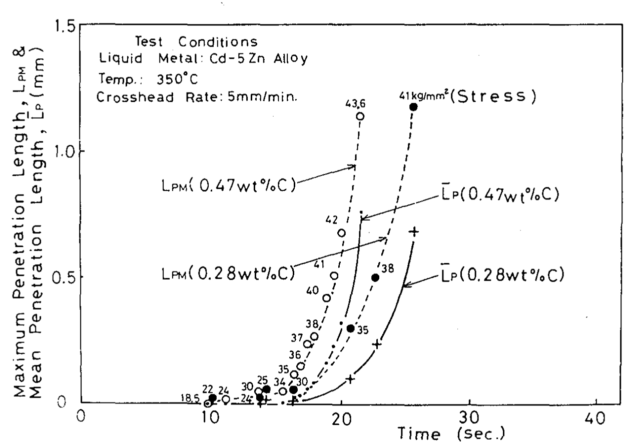

Fig. 9 Relation between maximum and/or mean penetration length and loading time

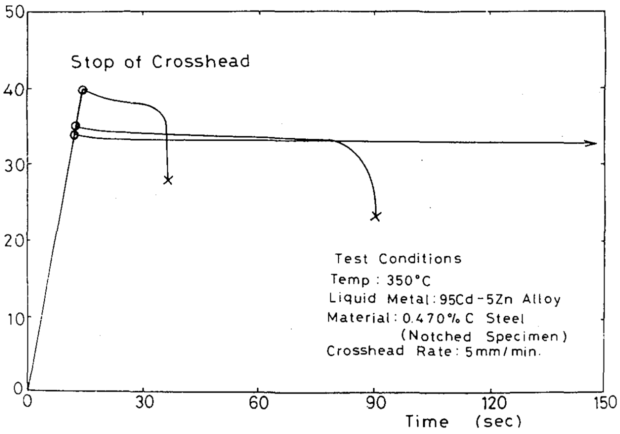

Fig. 10 Effect of penetration on stop of crosshead

the 34kg/mm^2 stress, LME did not occur in spite of the continual stressing for 30 minutes. We found that the value of the critical stress (35kg/mm^2) agreed with that of the start stress of the second stage. Thus, it was indicated that when LME occurs suddenly by the penetration of liquid metal into a carbon steel, the stress or load has to exceed a critical value.

3.3 Evaluation of Penetration Behavior at the Fracture

As pointed out earlier, the observation of fracture surface by optical microscopy was done after liquid alloy deposited on the surface was chemically removed. Figure 11 shows typical fracure surfaces of the various carbon steels (0.066%C, 0.28%C and 0.47%C) embrittled by liquid Cd-5Zn alloy. The sketches at the bottom in **Fig. 11** show regions hatched where a grain boundary penetration preferentially occurred and other regions were a ductile failure occurred. The onset site of the ductile fracture indicates where applied stress is abruptly lowered at the stress curve in Fig. 6. Moreover, it was observed that on the embrittled regions, the fracture surfaces are perpendicular to the tensile axis and show almost a plane surface. Thus, we measured the mean penetration length ($\bar{L}p$) on the fracture surface by the method as shown in Fig. 8. Next, we show that the mean penetration length is calculated using the maximum load of material itself without liquid metal, as shown below. The true stress(σ) at the ultimate tensile strength (nominal stress) (σ_0) is generally given by the following equation.

$$\sigma = \sigma_0 \ (1 + \varepsilon) \tag{1}$$

where ε is the strain at maximum load. With the notched specimen, it was directly obtained from the tensile test. By assuming that the fracture stress of

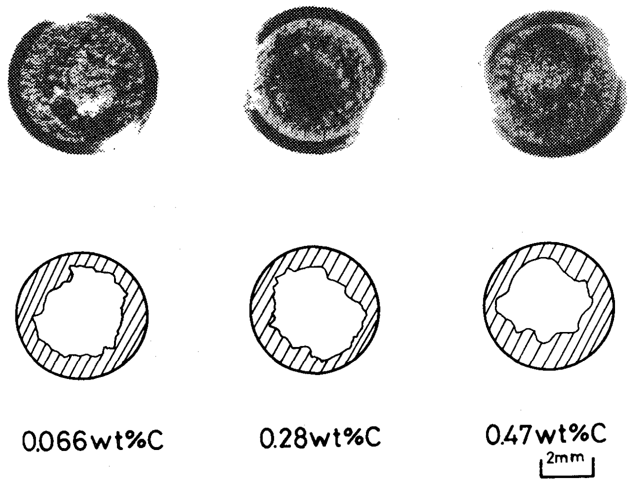

Fig. 11 Typical fracture surface appearances of various carbon steels deposited with liquid Cd-5Zn alloy and then chemically removed

steel with liquid metal is identical with the tensile strength of the material without liquid metal, the mean crossectional area (S) not embrittled with liquid metal is given by eg. (2).

$$S = \frac{Pmax.}{\sigma} \tag{2}$$

where Pmax is tha maximum load of steel in contact with liquid metal. Since the mean radious ($\bar{r}$) of the part unaffected by LME is $\sqrt{S/\pi}$, the mean penetration length($\bar{L}p$) is

$$\bar{L}p = r_0 - \bar{r} \tag{3}$$

where r_0 is the radious of the original tensile specimen.

Thus, the values of the mean penetration length measured experimentally from the fracture surfaces were then compared with the mean penetration length caluculated by the above-mentioned method. These results are shown in **Table 2**. For the notched and smooth speciments respectively, the calculated values of the mean penetration length show a good agreement with values obtained from the fracture surfaces. Therefore, it was proved that fracture stress of steel with liquid metal is identical with the tensile strength of the meterial without liquid metal. Consequently a final fracture with liquid metal occurs when the brittle zone goes over a critical area. In another words, the final fracture of LME occurs when the least section of specimen which is not embrittled can not stand against a maximum load of the material itself. It is associated with a ductile fracture. Thus, in duscussing the susceptibility of steel by LME, it is important to consider how far liquid metal penetrates inside of the substrate. In the next section, we shall

Table 2 Results of tensile tests for LME of steels

Materials		Liquid Metals (at.%)	Max. Load (Kg)	Mean Penetration Length (mm)	
C %	Specimen			Calculated	Measured
0.066	Smooth	95Cd-5Zn	897	0.464	0.461
	Notched		680	0.542	0.523
		50Cd-50Zn	550	0.663	0.674
0.280	Smooth	95Cd-5Zn	1200	0.508	0.555
	Notched		810	0.634	0.686
		50Cd-50Zn	700	0.766	0.778
0.470	Smooth	95Cd-5Zn	1348	0.710	0.682
	Notched		930	0.711	0.701
		50Cd-50Zn	785	0.831	0.835
0.028	Smooth	95Cd-5Zn	891	0.327	0.301
0.139			1074	0.488	0.491
		Pure Cd	1302	0.331	0.202
	Notched	95Cd-5Zn	735	0.616	0.620
		Pure Cd	1110	0.186	0.167

present more about this susceptibility to LME in some detail.

3.4 Evaluation of LME

Kamder[2] has pointed out that a prediction for the ductile or brittle behavior of solids by liquid metal discussed by kelly et al.[14] might be utilized for the occurrence of LME. The argument presented by Kamder is essentially as follows: when the interatomic force (σ_0) of solid metal and the shear stress (τ_0), are altered to σ and τ, respectively by contact with liquid metal, if the ratio σ/τ is smaller than the ratio σ_0/τ_0, LME occurs. Mclean[10] and Eborall et al.[11] have evaluated the grain boundary penetration by $2\gamma_{S-L}-\gamma_{GB}$, where γ_{GB} and γ_{S-L} are the grain boundary energy and the surface energy for a solid/liquid interface, respectively. However, these studies have been emphasized only for the occurrence of LME, and especially, in the latter case since it is presumed that the γ_{GB} may change under the stress, it may be considered that the results can not be utilized for the evaluation of the susceptibility on LME. On the other hand Rostoker et al.[1] have evaluated the sensitivity of various solid metals embrittled by liquid metals, using elongation (strain) to fracture, fracture time, tensile strength (load) etc. However, as LME[12] is the reduction in the ductility of stressed materials by contact with liquid metals, it may be convenient to evaluate the sensitivity of embrittlement by using the mean penetration length of liquid metal demonstrated in this study. Thus, this mean penetration length shows how fast a liquid metal penetrates along the grain boundary, and the tensile stress arrives at the intrinsic tensile strength under the constant strain, at which the material itself can not bear. Therefore, the embrittlement of various carbon steels can be evaluated by the mean penetration length at fracture as shown in Table 2. From this result, it is known that as the carbon cotent in carbon steels increases, the susceptibility of steels to LME increases. Moreover, as the amount of Zn to Cd increases, the susceptibility also increases.

4. Conclusions

Tensile tests were done in air and in liquid Cd-Zn alloys at 350°C, using both notched and smooth specimens of various carbon steels. The following conclusions were obtained concerning the penetration behavior by liquid metal and the susceptibility to LME:

1. By a grain boundary penetration of liquid metals during tenstile tests, the flow curves of various carbon steels are slightly altered.
2. For the faster penetration by liquid metal into carbon steel, the stress or load has to exceed a critical value.
3. Although the sensitivity of LME can not be evaluated only by the maximum load in liquid metal, it can be evaluated by using the mean penetration length.
4. The fracture stress by LME is identical with the tensile strength of the material itself.
5. Embrittlement of the liquid Cd-Zn alloy/carbon steel couples occurs with 100 percent probability in this experment and scatter of stress-strain curves is scarcely seen.

Acknowledgments

The authors would like to thank Dr. T. Yoshida and Mr. S. Sugiura, Meijo University, for helpful discussion and the Ministry of Education for supporting this study with a Grant-in-Aid for scientific research.

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