A SOLUTE PEAK ASSOCIATED WITH THE GRAIN BOUNDARIES OF IRON CONTAINING A SMALL AMOUNT OF CARBON

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Abstract.- Some investigations of the effect of interstitial so-
lute additions on the grain boundary peak were made in iron. At
the higher temperature side of the iron grain boundary peak, a
"carbon solute peak" appeared for iron containing 0.0002 wt% and
0.0005 wt% carbon. The activation energy for grain boundary re-
laxation in pure iron is 49±3 kcal/mol and that for the "carbon
solute peak" is equal to 85±4 kcal/mol. The solvent peak disapp-
eared as the amount of carbon increased up to 0.0027 wt%. There-
fore, it seems easy to explain the results given by Miles and
Leak that no solute peak appeared together with the solvent peak
in iron containing carbon and there was an abrupt change on the
curve of variation of activation energy for grain boundary damping
of iron with carbon content. The mechanism of solute peak was
discussed.

1. Introduction

It is well known that addition of the substitutional impurity re-
duced the height of the original grain boundary (G.B.) peak, called the
"solvent peak" and simultaneously a new "solute peak" occurred at a much
higher temperature. But previously published work on the solute grain
boundary peak has referred exclusively to substitutional impurity ele-
ments such as copper (1) and silver (2) alloys. The interstitial solu-
te peak have not yet been observed by others. The effects of intersti-
tial impurity on grain boundary peak have been studied by Miles and
Leak (3) for iron containing carbon and nitrogen. The peak height,
peak temperature and the activation energy all increased with small
additions of carbon or nitrogen and no isolated solute peak was obser-
ved. Maringer et al (4) had measured the influence of oxygen on the
grain boundary relaxation in molybdenum, no well-defined peak appeared
on the internal friction versus temperture curve. In our laboratory,
the grain boundary relaxation in molybdenum was studied (5)(6). When
the frequency of vibration is 1 cps, a pure Mo G.B. peak occurs around
1020°C, much the same as the result measured by Murray (7). This G.B.
peak is reduced by oxygen or carbon additions, but a solute peak

* An unpublished work made in 1966.

appears at much lower temperature on the same damping curve. "Oxygen peak" occurs around 890°C and "carbon peak" occurs around 925°C at 1cps We thought that the interstitial solute peak should also appear in iron containing carbon or nitrogen. Some investigations on this subject are reported here.

2. Experiment

The internal friction was measured with a torsion pendulum, the specimen and vibrating system were maintained in a high vacuum.

Electrolytic purity iron was used. Specimens were wires 20 cm long and diameter about 1 mm. Nitrogen and carbon were removed by prolonged heat treatment at 720°C in flowing moist hydrogen followed similar treatment in dry hydrogen. A required amount of carbon was added into the specimen by heating it at 600°C in a mixture of dry hydrogen and benzene. The treatment lasted between 10-15 minutes. The specimen loaded with carbon was homogenized by heating in vacuum for 7 hours and then quenched into cold water for determining the carbon content by the measurements of Snoek peak. Experiments showed that the carbon content had been added was well below the limit of solubility at 600°C.

The grain size was measured with a metallographic microscope.

3. Results and Discussion

The internal friction of pure iron specimen after removing carbon and nitrogen as a function of temperature was measured, as shown in Fig. 1, curve A, a grain boundary peak near 480°C of pure iron was observed, which has been confirmed by the same measurements with a specimen of gross grain (curve B). Curve C shows the results of iron wire containing 0.0002 wt% carbon, at the higher temperature side of the original pure iron solvent peak around 500°C, a new solute peak around 550°C due to carbon was observed. The solvent peak depressed while the solute peak increased with increasing carbon content (curve D).

The activation energy for each peak were determined: 49±3 kcal/mol for the iron solvent peak; 85±4 kcal/mol for the carbon solute peak. These are consistent with the results given by Miles and Leak (3) for pure iron and for iron containing carbon respectively, but they did not observe these two peaks simultaneously and concluded in the figure that the activation energy for the original solvent peak increased abruptly at first with the increase of the carbon content, and then decreased to a constant value. Probably because the lowest carbon content in the specimens they used was 0.009 wt%, the solvent peak was suppressed due to this carbon content. We have measured the G.B. damping of a speci-

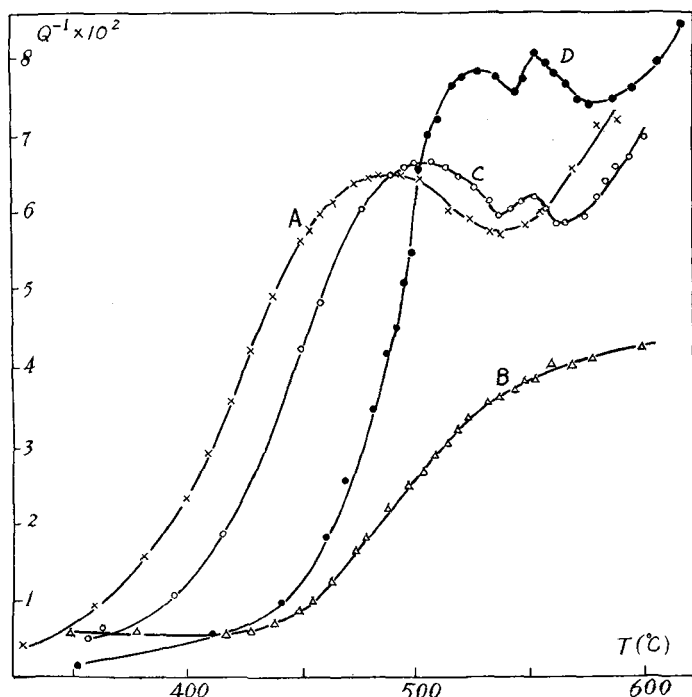men with carbon content up to 0.0027 wt%, almost only one peak was observed.

Fig. 1: Internal friction vs. temperature for polycrystalline Fe before and after successively adding carbon, showing G.B. peak of pure Fe and solute G.B. peak due to carbon, $f= 0.63$ cps

A. pure Fe,
   grain size:
   30 grain/mm

B. pure Fe,
   gross grain

C. 0.0002 wt%
   carbon,
   grain size:
   29 grain/mm

D. 0.0005 wt%
   carbon
   grain size:
   26 grain/mm

It was generally accepted that the grain boundary relaxation results from G.B. sliding blocked by the interlocking effect of grain corners or the ledges on the boundary. The earlist attempt at an atomistic theory was that of Ke (8), who proposed that the grain boundary was made up of local disordered groups and that the rate-controlling step of the sliding process involved the movement of a pair of atoms in such a group. Referring to this model and with the addition of the concept suggested by Sautter et al (9) that annealing of alloys produces two sets of boundaries:"solute sensitive" and"solute insensitive" boundaries, we can interpret that both the solvent and solute peak appear together on the same curve. The solvent peak corresponds to relaxation controlled by diffusion of solvent atoms alone in "solute insensitive" boundaries. The "solute sensitive" boundaries give rise to a solute peak, where some solvent atoms in the disordered group are substituted by solute atoms, the relaxation will be controlled by a diffusion with activation energy different from that of the former case and thus an isolated solute peak occurs.

Recently, some reviews on the development of models for G.B. damping have been reported (10)(11)(12). Roberts and Barrand (13)(14) pro-

posed a model for G.B. peak in pure metals in terms of a reversible dis-
location climb and/or glide process in grain boundaries. The concept
of individual grain boundary dislocation collecting a solute atmosphere
and their subsquent motion being controlled by solute diffusion, might
explain the appearance of a solute peak. The barrier to grain boundary
movement caused by the binding effect of solute atom to dislocation in-
creases the activation energy for G.B. relaxation, this coupled with an
increase in relaxation time, will give rise to the solute peak being ob-
served at a higher temperature. This model is compatible with the re-
sults of some substitutional alloys.

As already mentioned, a small amount of oxygen or carbon appearing
on the grain boundaries in Mo would give rise a solute peak (6) with the
peak temperature much less than that of G.B. peak in pure Mo. Fig. 2
shows the effect of oxygen on the G.B. peak in Mo. The peak at 1020°C
has been confirmed as the G.B. peak for pure Mo. (6) Because two peaks
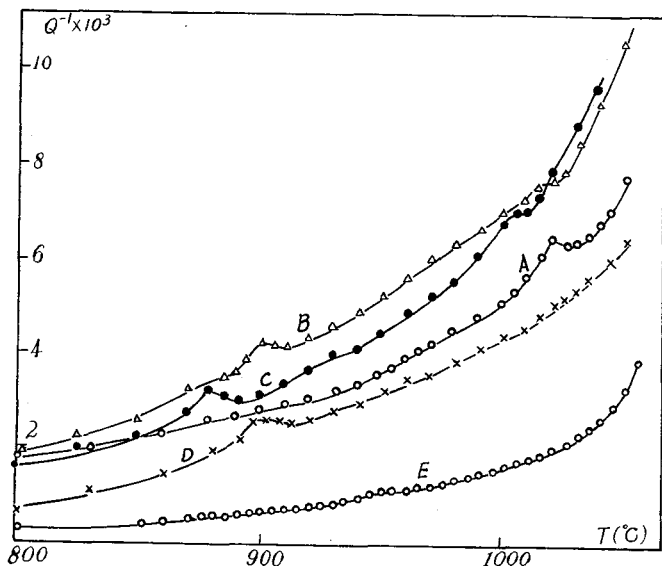
appeared together on the curves B and C for polycrystalline Mo dopped with oxygen whereas no peak was observed on curve E for oxygenated Mo single crystal, the peak at 890°C may be considered as the solute peak due to oxygen. The activation energy for this peak is about 80 kcal/mol, and that for the carbon solute peak is 98 kcal/mol (6).

Fig. 2: Internal friction vs. temperature for polycrystalline Mo(near
   spectroscopic purity) before and after the addition of oxygen.

   A. After the degassing treatment (annealing at 1700°C in hydrogen
      for 1 hour, then annealing at 1400°C in vacuum for 1 hour)
      f=1.2 cps

   B. After adding oxygen with wet hydrogen at 1200°C for 45 min.
      f=1.2 cps

   C. After the measurement B, change the frequency to f=0.67 cps

   D. After the measurement C, adding oxygen at 1300°C for 30 min.
      f=1.23 cps

   E. Mo single crystal after adding oxygen, f=0.55 cps

Both are less than 115 kcal/mol, the activation energy for pure Mo G.B.
peak. In addition, the "Bi peak" in Cu (15) due to the presence of Bi
at Cu grain boundaries has a peak temperature much less than that for
the pure Cu G.B. peak and it probably in turn has a somewhat smaller
activation energy than that of pure Cu peak. Therefore, the mechanism
for the solute peak attributed to the dislocation collecting a solute
atmosphere should be modified to involve this case.

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