

PULSED LASER TREATMENT AT Fe/C₆H₆ INTERFACE: A MÖSSBAUER EFFECT STUDY

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The pulsed ruby laser induced reactive-quenching process at Fe/C₆H₆ [benzene] has been investigated using conversion electron Mössbauer spectroscopy (CEMS). It is shown that iron carbide phases can be synthesized when an iron foil immersed in benzene is treated with ruby laser pulses ($\lambda = 694$ nm, pulse width ~ 30 ns, energy density = 15 J/cm²). The results indicate the formation of ϵ -carbide and Fe₅C₂ phases in the as-treated sample and its transformation to Fe₃C upon thermal treatment. The result of the CEMS measurements are supported by small angle X-ray diffractometry.

INTRODUCTION :

Thin films of compounds such as carbides, nitrides, oxides and oxynitrides find applications in diversified fields such as mechanical industry, magnetic industry and semiconductor technology. There are various methods to synthesize these compounds/1-2/. Recently, Patil et al./3/ proposed a new method to obtain metastable compounds through reactive-quenching process at liquid/solid interface, using pulsed laser treatment. Such a laser processing has an advantage that it can be easily adopted to technological needs and constraints.

In the present work we report on the formation of iron carbide phases by pulsed ruby laser-induced interface reactions between metallic iron and benzene. The microstructural characterization of the phases formed has been carried out using the technique of conversion electron Mössbauer spectroscopy (CEMS). In addition we have also used small-angle X-ray diffraction technique to supplement the information obtained on the basis of CEMS measurements.

EXPERIMENT :

Iron foils obtained from GoddFellow Metals [purity: 99.999%] were used in the present work. These foils were appropriately microetched prior to use and then treated with pulsed Ruby Laser pulse ($\lambda = 694$ nm, pulsewidth = 30 ns) at an energy density of 15 J/cm². In order to enhance the effects, each spot was irradiated twice. The iron foil laser treated under benzene was subjected to vacuum annealing at different temperatures in the range between 200° C to 500° C for thirty minutes in each case. The CEMS spectra were recorded at room temperature using a constant acceleration Mossbauer set up with ⁵⁷Co:Rh as source/4/. The small angle X-ray diffraction (XRD) patterns were obtained on a Rigaku (Japan) machine by keeping the glancing angle of incidence fixed at 2°.

RESULTS AND DISCUSSION :

The CEMS spectrum of the as-received iron foil appears as shown in Fig.1(a) and it shows a single sextet contribution due to α -Fe with an internal magnetic field [IMF] value of 330 kOe. The CEMS spectrum corresponding to the iron foil laser treated under an liquid benzene at an energy density of 15 J/cm² is shown in Fig.1(b). This spectrum is significantly different as compared to the spectrum of Fig.1(a) and it can be resolved in to the following subspectral components:

- (a) Doublet : Isomer shift (I.S.) = 0.27 mm/sec
 Quadrupole splitting (Q.S.) = 0.96 mm/sec
 (b) Sextet : I.S. = 0.28 mm/sec,
 Internal Magnetic field (IMF) = 268 kOe.
 (c) Sextet : I.S. = 0.29 mm/sec, IMF = 213 kOe
 (d) Sextet : I.S. = 0.34 mm/sec, IMF = 190 kOe
 (e) Sextet : I.S. = 0.07 mm/sec, IMF = 327 kOe

The doublet and sextet with IMF of 268 kOe together correspond to the ϵ -carbide (ϵ -Fe₂C) phase [5]. The ϵ -carbide phase has the hexagonal closed packed structure with interstitial carbon atoms in octahedral interstices. The sextets (c) and (d) together represent the presence of Fe₅C₂ phase (Hagg carbide) which has a orthorhombic crystal structure [5]. In principle, three different IMF values of about 222 kOe (I.S.= 0.35 mm/sec), 184 kOe (I.S.= 0.30 mm/sec) and 110 kOe (I.S.= 0.30 mm/sec) are expected for this phase arising from three different non-equivalent iron sites and these sites have a population ratio of 2:2:1. In our case, the non-observance of the weaker sextet may be due to the fact that

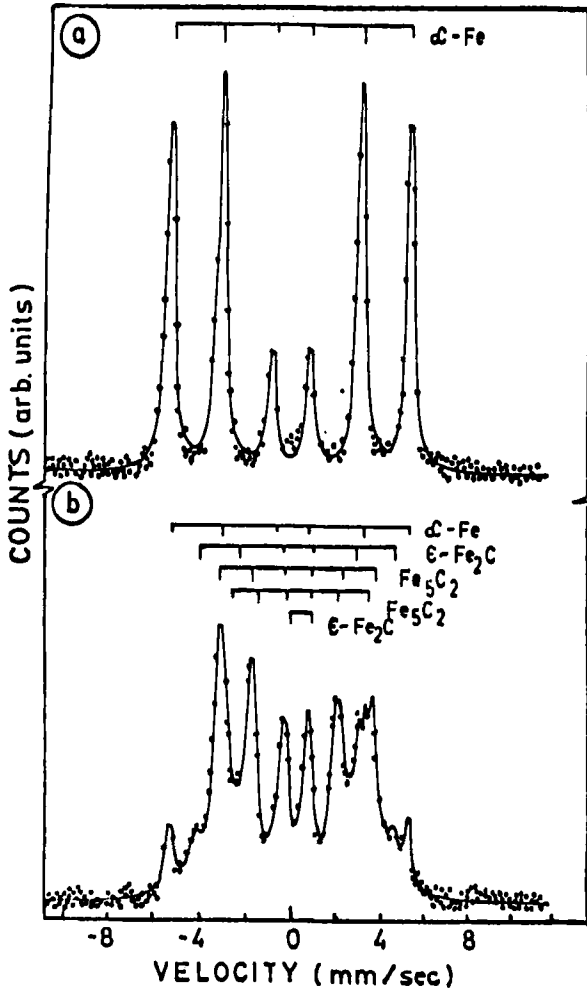


FIGURE 1 : Room temperature CEMS spectra of (a) as-received iron foil and (b) iron foil laser treated under Benzene at an energy density of 15 J/cm².

the Fe₅C₂ phase which is formed after the pulsed Laser treatment is not completely ordered and has vacancies on the corresponding sublattice.

In order to confirm the formation of ϵ -Fe₂C and Fe₅C₂ phases in the treated sample we performed small angle X-ray diffraction (XRD) measurements (Fig.2). The analysis of different diffraction peaks indicate the formation of ϵ -carbide, Fe₅C₂ and Fe₃C phases. However, the contribution of Fe₃C in the CEMS spectrum of laser treated sample could not be discerned because its hyperfine interaction parameters closely overlap with those for Fe₅C₂ phase.

The CEMS spectrum of the sample annealed at 200^o C for half an hour is shown in Fig.3(a) and can be fitted with five sextets, the hyperfine interaction parameters being as under:

- (a) I.S.= 0.06 mm/sec, IMF = 341 kOe
- (b) I.S.= 0.23 mm/sec, IMF = 242 kOe
- (c) I.S.= 0.30 mm/sec, IMF = 216 kOe
- (d) I.S.= 0.26 mm/sec, IMF = 186 kOe
- (e) I.S.= 0.32 mm/sec, IMF = 122 kOe

The sextet with IMF of 242 kOe corresponds to the ϵ -carbide phase retained after thermal annealing. Clearly, the sextets (c), (d) and (e) together represent the Fe₅C₂ phase, while the sextet (a) represents α -Fe. The appearance of the weaker sextet having IMF of 122 kOe corresponding to the third site of Fe₅C₂ phase clearly indicates the precipitation of well defined Fe₅C₂ phase.

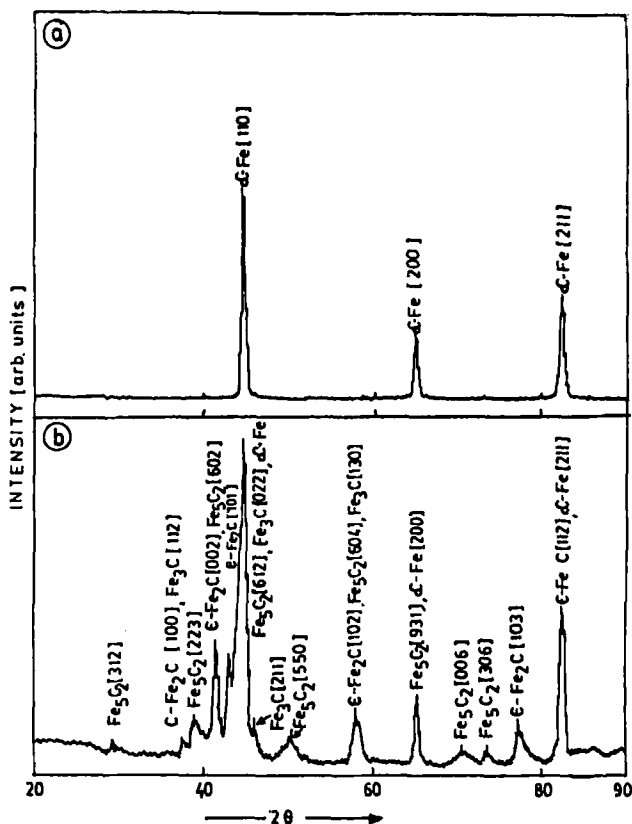


FIGURE 2 : Small angle x-ray diffraction patterns for (a) as-received iron foil treated under Benzene at an energy density of 15 J/cm².

On further annealing at 400°C for half an hour, one observes the CEMS spectrum as shown in Fig.3(b). The CEMS spectrum can now be fitted with three sextets having the following values of hyperfine interaction parameters.

(a) I.S.= 0.04 mm/sec, IMF= 327 kOe

(b) I.S.= 0.08 mm/sec, IMF= 189 kOe

(c) I.S.= 0.27 mm/sec, IMF= 200 kOe

The sextet (a) is once again due to α -Fe. The sextet (b) is attributed to Fe₅C₂ phase. The absence of two sextets [with an IMF of 213 kOe and 120 kOe] corresponding to this phase and the appearance of the sextet (c) corresponding to Fe₃C reveals the partial transformation of Fe₅C₂ phase to Fe₃C phase.

The CEMS spectrum of the sample annealed at 500°C is shown in Fig.3(c). This spectrum shows precipitation of α -Fe with small contribution of Fe₃C phase. This suggests that above 400°C thermal diffusion of carbon atoms allows them to migrate away from the modified surface. Such a relatively low temperature might suggest that the carbide in the as-treated sample is present in the form of small precipitates surrounded by γ -Fe rather than as a uniform layer.

CONCLUSION :

We have presented a new method to synthesize iron carbide phases on the surfaces of metallic iron. The iron foil laser treated under benzene shows the formation of ϵ -carbide and Fe₅C₂ phases. On annealing at 500°C, precipitation of α -Fe along with small contribution of Fe₃C phase is seen.

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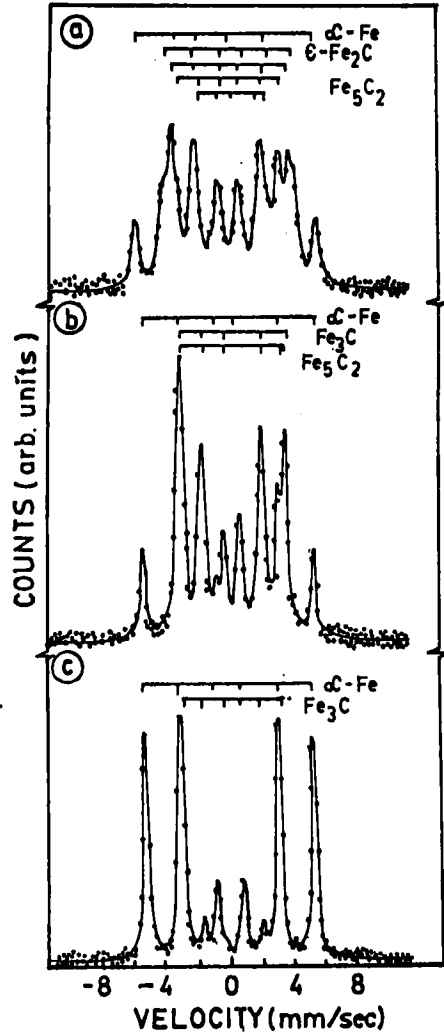


FIGURE 3: CEMS spectra of iron foil laser treated under benzene and annealed at (a) 200°C, (b) 400°C and (c) 500°C.