AMORPHIZATION OF C-IMPLANTED Fe(Cr) ALLOYS

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ABSTRACT

The amorphous phase formed by implanting C into Fe alloyed with Cr, which is a prototype for the amorphous phase formed by implanting C into stainless steels, is compared to that formed by implanting C plus Ti into Fe and steels. The composition range of the phase has been examined; higher Cr and C concentrations are required than needed with Ti and C. The friction and wear benefits obtained by implanting stainless steels with C alone do not persist for the long durations and high wear loads found with Ti and C. However, the amorphous Fe-Cr-C alloys exhibit good aqueous corrosion resistance.

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1. Introduction

Ion implantation can be used to form metastable surface alloys which may have beneficial properties, such as increased resistance to wear or corrosion, making such treatments attractive for technological applications. Implantation of sufficient concentrations of both Ti and C into Fe or steels [1-4] produces an amorphous surface layer which has been shown to greatly improve tribological properties. More recently, we found that a similar amorphous phase can be formed by implantation of C alone into alloys containing Cr, such as stainless steels [1,5].

Since we found similar amorphous layers when C was implanted into binary bcc alloys (Fe-12, 18 at.% Cr), as well as fcc (304, 19 at.% Cr) and bct (martensitic 440C, 17 at.% Cr) stainless steels [5], the amorphous phase in Fe-Cr alloys is taken as a prototype for the amorphous phase in the steels. We have characterized the composition range of the amorphous phase with transmission electron microscopy (TEM) and ion beam analysis for bulk Fe-Cr alloys with 6, 12, and 18 at.% Cr after 15-keV C implantation at room temperature. The results indicate that Cr plays a similar role to Ti in stabilizing the amorphous phase, but larger concentrations of Cr and C are required than those of Ti and C. However, the tribological properties of the amorphous phase formed by implanting 440C with C were examined and found to be less beneficial than those of layers implanted with Ti and C. The electrochemical properties of the C-implanted Fe-Cr alloys were also investigated, and improved corrosion resistance was found relative to the unimplanted alloys.

2. Amorphous Phase Composition Range

The three Fe-Cr alloys were prepared by melting high purity Fe and Cr to produce an initial ingot, followed by several re-melts in vacuum. Ingots

were hot and cold rolled to produce the material used in this study. Samples were prepared for TEM by backthinning with jet electropolishing using a nitric acid-methanol solution. For 12 and 18 at.% Cr alloys implanted with sufficiently high C concentrations, this produced a free-standing surface layer composed of the amorphous phase and an oxide phase. Figure 1 shows a transmission electron diffraction pattern obtained from such a surface layer on an Fe-12Cr sample (12 at.% Cr) implanted with 1.1×10^{17} C/cm² at 15 keV. The pattern shows diffuse rings due to the amorphous phase and sharp rings which identify the oxide as Fe₃O₄ (magnetite) [6]. Alloys with 6 at.% Cr did not contain the amorphous phase after implanting up to 45 at.% C, but instead contained the hexagonal carbide phase ϵ -Fe₂C, which is also found when pure Fe is implanted with C [4].

The composition of each sample was obtained using ion backscattering spectrometry with 6 MeV He⁺. The C profiles were deduced by fitting the spectra with the RUMP analysis program [7] using the enhanced cross-section found for C at this energy [2]. For the sample of Fig. 1, this procedure showed a peak C concentration of 28 (± 3) at.% at a depth of 20 nm, with a fall-off to half maximum at 40-50 nm. Total areal densities of C and O were also measured for each sample using nuclear reaction analysis with the $^{12}\text{C}(\text{d,p})^{13}\text{C}$ and $^{16}\text{O}(\text{d,p})^{17}\text{O}$ reactions and a 0.9 MeV deuterium beam. The total C in the samples agrees well with the implanted dose, indicating that extra C is not incorporated into the sample during the implantation. This result contrasts with the additional C found to be incorporated from residual vacuum gases during Ti implantation [2]. The total O detected in these samples increased from $\sim 3 \times 10^{16}$ O/cm² for an unimplanted sample to $\sim 8 \times 10^{16}$ O/cm² for the implantation of 2×10^{17} C. These O contents were

consistent with Fe_3O_4 surface oxides (typically 10 nm thick) used in the RUMP simulations to obtain composition profiles.

The combination of ion-beam compositional analysis and TEM phase determination allows a ternary phase map to be constructed, showing the approximate boundary between crystalline phases and amorphous material. Such a map constructed from our data for Fe-Cr-C alloys [5] is shown in Fig. 2(a), with the comparable map from our earlier work with Fe-Ti-C alloys [2,4] shown in (b). Filled symbols represent peak concentrations for which an amorphous surface layer was observed, while open symbols represent compositions which were observed to be crystalline. The half-filled symbol represents a borderline composition. Included in both maps (on the C axis) is the crystalline state (Fe_2C) found for pure Fe implanted with C [4].

These results indicate that Cr plays a similar role in stabilizing the amorphous phase to that of Ti in amorphous $\text{Fe}(\text{Ti},\text{C})$. However, there are significant differences. Stabilization of the amorphous layer clearly requires a higher concentration of C as well as a higher Cr content than needed with Ti and C. For example, ~20 at.% C is needed with 18 at.% Cr, while only ~4 at.% C is needed with 18 at.% Ti. The increased stability of the amorphous phase with Ti may be due to its stronger bond with C than that of Cr, or to the lower liquidus temperature of Fe-Ti relative to Fe-Cr [9].

3. Tribology of Amorphous Phases

One of the motivations for studying near-surface alloying with ion implantation is to search for cost-effective treatments which produce substantial tribological benefits. The amorphous alloys produced in stainless steels by C implantation appear to be similar to those in the Ti + C treatment. Since implanting C alone would be considerably cheaper

and permit thicker layers to be formed in comparison to the Ti + C treatment, we explored their tribological properties with pin-on-disk testing.

A summary of the results for 440C is shown in Fig. 3, which compares the friction coefficients observed after 1000 cycles for pin loads from 10 - 1000 g for unimplanted steel to those for implantation of C alone and to those for the earlier Ti + C treatment. The C treatment (2×10^{17} C/cm², 30 keV) produces a C profile which peaks at 37 at.% at a depth of 50 nm and falls to half this value at 90 nm [1], while the Ti + C treatment [3] produces concentrations of ~20 at.% for both Ti and C over comparable thicknesses. The tests show that the C implantation is effective in reducing friction only at very light loads (≤ 25 g), which are much less than those for which benefits are obtained with Ti + C (≤ 600 g). Higher and lower fluences of C alone (1 and 3×10^{17} C/cm², respectively) did not significantly change this result. These comparisons indicate that Ti is needed in these amorphous alloys for extended reductions in friction and wear. It is noted that other studies indicate that Ti alone does not give the extended benefits; both Ti and C are required [1].

4. Corrosion of Amorphous Phases

Another motivation for studying these surface treatments is the possibility of improving the resistance to aqueous corrosion. The present treatment with C alone substantially improves corrosion resistance, as can be seen in Table I, which shows characteristic numbers from potentiodynamic polarization measurements. All three Cr compositions were examined.

For the Fe-6Cr alloy the comparison is between corrosion of the unimplanted alloy and a sample implanted with 2×10^{17} C/cm². Both the

implanted and unimplanted surfaces exhibit active dissolution, with almost no real passivity. The passive current density is about two orders of magnitude lower for the implanted alloy compared to the base alloy, indicating that the C implantation has improved the corrosion behavior of the alloy. An increase in open circuit potential (an increased tendency toward passivity) is also seen. These improvements are significant for an alloy with such a low Cr content.

For the Fe-12Cr alloy, the comparison is between samples implanted with 0.2 and 1.3×10^{17} C/cm². The low fluence sample exhibits an active peak at around -400 mV SCE (saturated calomel reference electrode) with a current density of 3×10^{-3} A/cm². The high C sample, in contrast, exhibits no active dissolution at all. The current is cathodic throughout the entire scan, and becomes anodic only at 1.0 V, where oxygen evolution is observed. These results indicate that the surface implanted with the higher C fluence provides a substantially improved corrosion resistance.

No active dissolution is observed for the Fe-18Cr alloy implanted to 1.1×10^{17} C/cm² either, but the corrosion rate for this alloy, with so much Cr, is already very low. The trend, however, is still present. C implantation shifts the open circuit potential in the noble direction and induces spontaneous passivity.

5. Summary

Alloys containing sufficient Cr, including stainless steels, can be amorphized by the implantation of C to sufficient fluences [5]. We have compared the properties of these amorphous phases to those of the similar amorphous layers formed by implanting both C and Ti into Fe or steel. We find that the Cr-stabilized amorphous phase requires more Cr and/or C than

the Ti-based phase, and that the Fe-Cr-C amorphous phase gives much less tribological benefit than the corresponding Fe-Ti-C phase. The corrosion resistance of the Fe-Cr-C surfaces are substantially improved over the unimplanted alloys.

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Table I. Potentiodynamic polarization values for C implanted Fe-Cr

alloy	C implant	max current	open circuit potential	passive current
Fe-6Cr	unimplanted	1.0 E-2	-0.50	5.0 E-2
	$2.0 \times 10^{17}/\text{cm}^2$	0.1 E-2	-0.60	5.0 E-4
Fe-12Cr	$0.2 \times 10^{17}/\text{cm}^2$	0.5 E-2	-0.60	1.0 E-6
	$1.3 \times 10^{17}/\text{cm}^2$	0.0	1.00	0.0 *
Fe-18Cr	$0.2 \times 10^{17}/\text{cm}^2$	5.0 E-6	-0.25	1.0 E-6
	$1.1 \times 10^{17}/\text{cm}^2$	0.0	1.00	0.0 *

* no anodic dissolution

Figure Captions

- Fig. 1. Electron diffraction pattern taken from the free-standing amorphous surface layer on Fe-12Cr implanted with 1.1×10^{17} C/cm² at 15 keV. Diffuse rings from the amorphous phase are seen with superimposed sharp rings and arcs from Fe₃O₄ (magnetite).
- Fig. 2. Ternary phase maps showing the boundary between crystalline phases and amorphous for (a) Fe-Cr-C alloys, and (b) Fe-Ti-C alloys.
- Fig. 3. Friction coefficients observed after 1000 cycles of unlubricated pin-on-disk testing with 440C pins (0.79 mm radius of curvature) on fully hardened 440C steel disks in the unimplanted, C-implanted, and Ti + C-implanted conditions, plotted versus pin load.

Unlubricated pin-on-disc

440C discs
440C pins

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