Hyperfine Interact (2017) 238:55
DOI 10.1007/s10751-017-1425-7

Mössbauer and XRD characterization of the effect of heat treatment and the tribological test on the physical and mechanical properties of a Fe-Mn-Al-C alloy

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Abstract In this study, a Fe-29.0Mn-6.0Al–0.9C-1.8Mo-1.6Si-0.4Cu (Wt. %) alloy was prepared in an induction furnace. The as-cast sample was submitted to homogenization at 1050 °C over 8 hours, which was followed by quenching, and an aging heat treatment at 500 °C for 12 h. Wear tests were performed by using a Pin on Disk Tribometer (ASTM G99) at room temperature to evaluate the mass loss. Optical Microscopy, X-Ray Diffraction, and Transmission Mossbauer Spectroscopy were used to characterize the microstructure and structural properties of the samples. The obtained microstructure of the heat-treated samples was of the austenitic type, and their XRD patterns were refined with the lines of the austenite, martensite, galaxite, and FeO structures. Mössbauer spectra of powders, obtained from the surface of the samples, showed the presence of a broad doublet, which corresponded to the disordered austenite; and a small hyperfine magnetic field distribution associated with the disordered and ferromagnetic martensite. After the tribology test, the surface of the sample was examined, and it was obderved that the austenite, martensite, and galaxite

This article is part of the Topical Collection on *Proceedings of the 15th Latin American Conference on the Applications of the Mössbauer Effect (LACAME 2016), 13–18 November 2016, Panama City, Panama*
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Published online: 04 May 2017

phases were present. The martensite quantity increased and, those of galaxite and austenite decreased, but that of austenite appeared to have larger lattice parameter. The decrease in the galaxite content was a direct consequence of the wear test, which removed matter from the sample surface. The appearance of additional martensite was due to the transformation of the austenite by mechanical work. The additional presence of a new austenite with a bigger lattice parameter and of the Fe oxide was the consequence of the heating process of the sample during the tribological test. The Mossbauer spectrum of this sample confirms the increase of the martensite content. The mechanical properties increased with the heat treatment.

Keywords Fermanal steels · Heat treatment · XRD · Mossbauer spectrometry · Tribology

1 Introduction

Fe-Mn-Al-C steels have been used since the beginning of the second half of the last century as, possible substitutes for stainless steels based in Cr-Ni, due the smaller costs of their alloying elements and comparable, and in some cases, better mechanical properties [1, 2]. They have specific weight values that are approximately 13% lower than those of conventional stainless steels [3–5]. These steels are called high resistance advanced steels [1] or Fermanal steels [6–8] and have significant advantages in their mechanical properties in relation to carbon steels and conventional manganese or Hadfield steels [9]. Additionally, the Fe-Mn-Al-C alloy system permits, with some flexibility, the control of the plastic deformation mechanisms, which make possible to obtain a stress resistance and ductility, which are larger than those of conventional Mn steels, Ti alloys or carbon steels.

To obtain good mechanical properties, the most commonly used treatment is that involving quenching from temperatures at which the austenitic field is stable and subsequent aging for 16 h at 550 °C [2]. Many reposts have discussed the corrosive [10, 11], mechanical [12], and microstructural [13, 14] properties of Fermanal alloys. The effects of heat treatments and, addition of alloy elements to achieve precipitate hardening or solution hardening have also been reported [15]. Depending on the heat treatment and composition, Fermanal alloys can present with yield strength values, ranging from 825 to 1240 MPa and ultimate strengths values from 550 to 970 MPa [12]. Additionally, Fermanal alloys also show good elongation values, ranging from 30 to 60%. In some cases, these properties are better or similar to those shown by stainless steels.

Rodríguez [7] and Pérez et al. [8] reported the study of the effect of adding Cu on the corrosion resistance of Fermanal steels. They submitted Fermanal steels with and without Cu, autopasivable steels and pure Fe, to several wet and dry cycles in a SO_2 atmosphere. They found that after 18 cycles, Fermanal doped with Cu gained four times lesser weight than Fermanal without Cu, twenty times less weight than the autopasivable steel, and thirty five times less than pure Fe. This was the reason for adding Cu to a Fermanal alloy in a previous study published by the authors [16] as well as in this study.

Only a few studies about the tribological behavior of Fermanal steels have been published. Zudeima et al. [17] evaluated the effect of adding Al and C on the abrasive wear resistance of a Hadfield steel. For high strain and high Al as well as low carbon contents, the resistance increased due the increase in C solubility when the Al content increased For a low strain, the increase in the Al content decreased the abrasive wear resistance due to the formation of coarse grains. Huang et al. [18] performed wear tests in air of Fe-Mn-Al-C

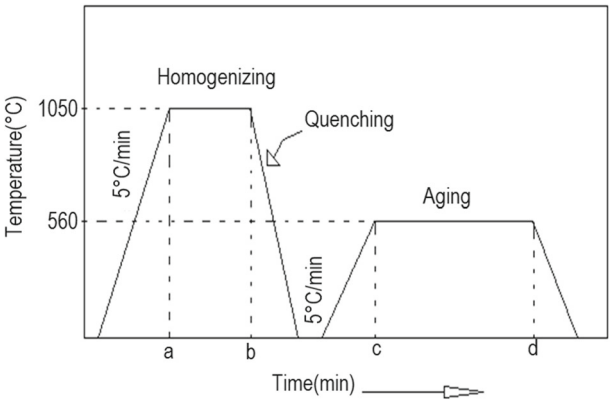

Fig. 1 Heat treatment cycle for "Fermanal" steel

steels with a load of 76 N. They showed that a solubilized sample presented a loss of matter, which was double that of an aged sample. This was due to the increase in the hardness and the presence of β-manganese phase inside the austenite matrix. Recently, the authors reported a study on the as cast Fe-29.0Mn-6Al–0.9C-1.8Mo-1.6Si-0.4Cu (Wt. %) alloy after it was melted in an induction furnace. The as cast sample presented a majority fraction of austenite, and a small quantity of martensite. After a tribological test, the martensite fraction increased, improving its mechanical properties and wear behavior [16].

This research aims to approach similar to that of previous study [16] in a heat-treated Fe-28.60Mn-6.00Al–0.86C-1.81Mo-1.59Si-0.43Cu (Wt. %) sample, to determine if a heat treatment improves the mechanical and tribological properties.

2 Experimental procedure

The raw materials and melting process used for the preparation of the as-cast Fermanal alloy, with a final composition Fe-29.0Mn-6Al-0.9C-1.8Mo-1.6Si-0.4Cu (Wt. %), are described in Ref. [16]. The as-cast sample of the previous report, which had an ingot shape, was submitted to homogenization treatment and placed in a furnace at room temperature (RT), and the temperature (T) was increased at a rate of 5 °C per minute until 1050 °C. Then, the sample was maintained at this T for 8 hours, which was followed by quenching in water. After-wards, the sample placed in the furnace for an aging treatment while increasing the T at a rate of 5 °C per minute until 550 °C; this T was maintained for 12 hours. Finally, the furnace was turned on and closed for 12 hours. Figure 1 illustrates the heat treatment used for the studied sample.

From the aged ingot, disks were cut for metallographic analyses, wear tests, and X Ray Diffraction (XRD) studies. These disks were sanded and polished until obtaining a mirror surface. One metallographic specimen was etched with nital for 20 s and cleaned with a 10% hydrochloric acid solution. Then, its surface was characterized by using Metallurgical Optical Microscopy (MOM). Pin on disk tribometer (ASTM G99) was used for the wear resistance measurement. The ball specimen was Cr steel (diameter 6 mm) with an applied load of 5N, sliding speed of 15 cm/s, and sliding distance of 1000 m. The wear test

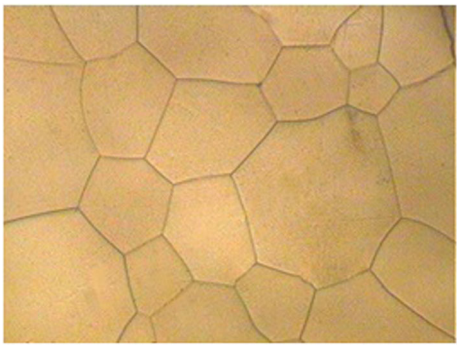

Fig. 2 Microstructure of Fermanal at 50X that was homogenized for 8 h and quenched in water

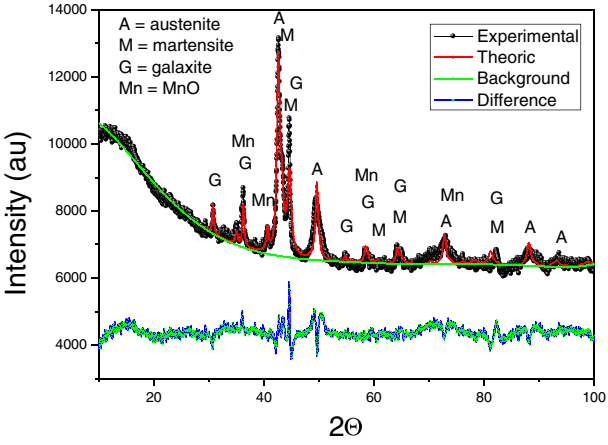

Fig. 3 XRD pattern of the aged Fermanal sample

was performed at room temperature. The XRD patterns were collected with a X'Pert PRO PanAnalytical diffractometer using the K_α lines of Cu, and the XRD patterns were refined with the GSAS program [19] while using a LaB_6 powder as the calibration sample. Transmission Mössbauer Spectra (TMS) of powdered samples, obtained by filling the surface of one disk, were taken using a 57Co (Rh) source and using an α-Fe foil as the calibration sample. The spectra were fitted with the MOSFIT program [20]. Hardness tests on the alloy surfaces were performed in different preparation conditions, using Brinell Hardness Tester, where a 50 N indentation load and time of 15 s were used. The XRD, Mössbauer, and hardness studies were performed before and after the wear test.

3 Experimental results and discussion

Figure 2 shows a micrograph of the Fermanal sample at 50X, after heat treatment at 1050 °C for 8 h and then quenching in water at 15 °C. This micrograph shows that this treatment contributes to the stabilization of the austenitic structure, which presents large grain sizes without segregations. It can also be noted that the grains are very symmetric.

Table 1 XRD parameters obtained from the refinement of the aged Fermanal pattern

Phase	Spatial group	Structure	Lattice parameters (Å)	Crystallite size (nm)	Wt. Fraction
Austenite	Fm3m	FCC	a = b = c = 3.6755±0.0001	14.81±0.03	46.56±0.02
Martensite	I4/mmm	Hexagonal	a = b = 2.8754±0.0002	11,28±0.02	28.56±0.03
			c = 3.0608±0.0002		
Galaxite	Fd3m	Cubic	a = b = c = 8.1962±0.0001	22.74±0.04	18.71±0.04
MnO	Fm3m	FCC	a = b = c = 4.4480±0.0001	20.35±0.05	6.17±0.03

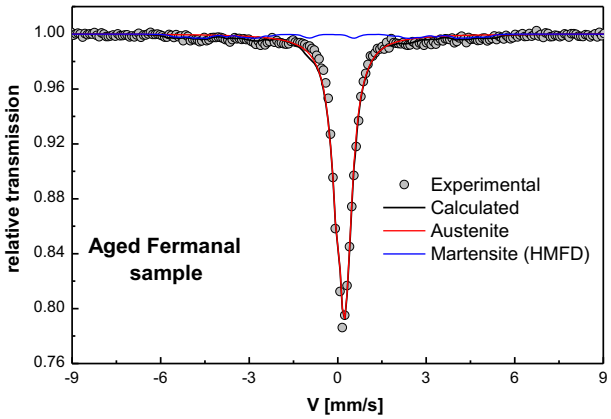

Fig. 4 MÖSsbauer Spectrum Of The Aged Fermanal Sample

The Brinell hardness of the obtained sample, after the homogenization heat treatment, was 415, which is larger than that of 355 obtained for the as-cast sample, which had the same composition with a dendritic morphology [16]. The obtained hardness after the aging treatment was 452, showing that this additional heat treatment improves the hardness.

Figure 3 shows the XRD pattern of the Fermanal sample after the aging process. The pattern was refined with the Crystallographic Information Files (CIFs) of the austenite, martensite, galaxite and MnO phases. These results contrast with those reported for the as-cast sample [16], in which the austenite (∼92 Wt. %) and martensite (∼8 Wt. %) phases were obtained. In the current study, for the aged sample, higher level of martensite (∼29 Wt. %, see Table 1), galaxite and MnO phases were obtained. The additional martensite explains the increase in the hardness obtained for the aged sample compared to the homogenized and quenched sample. As reported by Agudelo et al. [11] on the effect of the corrosion process of Fermanal samples in dry and wet cycles in SO_2 atmosphere, there was emigration of Mn atoms toward the surface, forming a self-sparking layer. In this way, some Mn atoms combined with Al and O to form galaxite and others combined with O to form the MnO. Galaxite is a mineral of the Al spinel group with the formula $MnAl_2O_4$ (pure galaxite) and, in some cases it can appears as $(Mn,Fe,Mg)(Al,Fe)_2O_4$ [21] or $Mn_{0.7}Al_{1.7}Fe_{0.5}O_4$ [22].

In Table 1, the XRD parameters obtained are reported, for the different phases, from the refinement of the pattern of the aged Fermanal sample.

As can be noted in Table 1, the mean crystallite sizes of the different phases are of the nanometric scale and are smaller than those of the homogenized sample, which are of

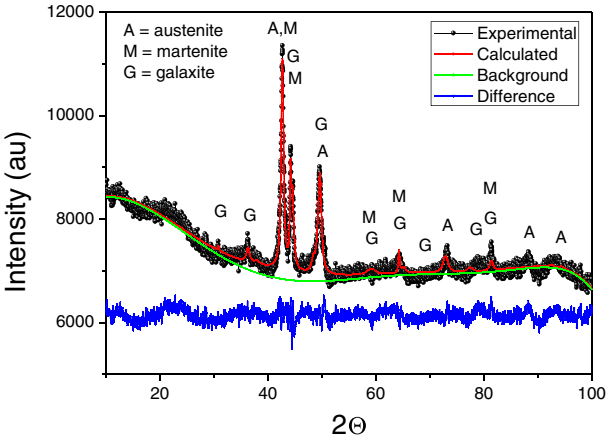

Fig. 5 XRD pattern of the aged and wearied Fermanal sample

Table 2 XRD parameters obtained from the refinement of the aged and wearied Fermanal pattern

Phase	Spatial group	Structure	Lattice parameters (Å)	Crystallite size (nm)	Wt. Fraction
Austenite	Fm3m	FCC	a = b = c = 3.6660±0.0001	14.30±0.03	48.22±0.02
Martensite	I4/mmm	Hexagonal	a = b = 2.8496±0.0002	37.95±0.03	
			c = 3.0965±0.0002	17,24±0.02	
Galaxite	Fd3m	Cubic	a = b = c = 8.1936±0.0001	49.15±0.04	13.83±0.04

micrometric scale (see Fig. 1). This can be explained as an effect of the ageing treatment, which permits the precipitation of new stable phases, with treatment at 550 °C. The mean refined perpendicular and parallel crystallite sizes are similar, showing a symmetric shape of the crystallites.

Figure 4 shows the Mössbauer spectrum of the aged Fermanal sample. This spectrum was fitted using a broad doublet, which corresponds to the disordered paramagnetic austenitic phase with a majority spectral area, and a Hyperfine Magnetic Field Distribution (HMFD), which corresponds to the disordered ferromagnetic martensite phase. This result differ from that reported for the as-cast sample, because martensite appears.

The small spectral area of the martensitic phase (9.67%) indicates that the majority of Fe atoms are inside the austenitic phase. The Mössbauer parameters of these phases are nearly the same as those obtained for the as-cast sample [16]. Galaxite, which was detected by XRD, doesn't appear in the MS, showing that in the aged sample this phase appears as $MnAl_2O_4$ (pure).

Finally, a disk of the aged Fermanal sample was submitted to a wear test using Pin on Disk equipment, in similar conditions as those used for the as-cast sample [15]. Figure 5 shows the XRD pattern of the aged and wearied sample, which was collected in the mixed region between the tested and not tested one.

The pattern was refined with the CIFs of the austenite, martensite and galaxite phases, and their crystallographic parameters are reported in Table 2. In this case, the MnO phase was not obtained indicating that this phase was in the surface of the aged disk and that the polish and wear test removed it.

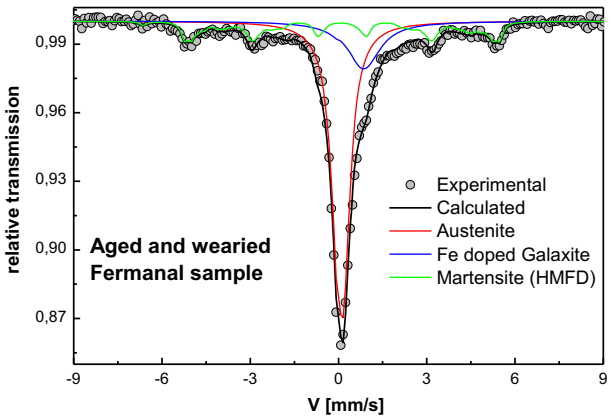

Fig. 6 Mössbauer spectrum of the wearied Fermanal sample

From Table 2, it can be observed that the martensitic weight fraction is larger than that of the aged sample and that of the galaxite decreases, indicating that the test induced an additional martensitic transformation. Additionally, galaxite is, in part, removed from the tested region. This test confirms that galaxite is formed on the surface of the sample by the migration of Mn atoms to the surface, and that its depth is greater than that of the MnO.

The obtained crystallite sizes are larger than that reported in Table 1 for the aged Fermanal sample, which is due to the increase of T during the wear test, which behaves as a heat treatment.

The Mössbauer spectrum of powder obtained from the surface of the tested sample is shown in Fig. 6. This spectrum was fit with two broad singlets, one associated with the austenite phase (65.5%) and the other, the broader one (14.5%), associated with a Fe doped galaxite [21], and the HMFD of the martensite (20.0%). The Fe doped galaxite was proposed in accord with the XRD results of this sample, which report this phase, as well as considering that this singlet presents Mössbauer parameters of δ ~0.93 mm/s and Γ ~1.92 mm/s. The Mössbauer study reported by Bluncson et al. [21] showed that Fe doped galaxite $(Mn_{0.7}Al_{1.7}Fe_{0.5})O_4$ presents Mössbauer parameters of a δ between 0.90 to 0.94 mm/s and ΔQ between 1.13 to 1.85 mm/s. Last results permit us to postulate that the broadest singlet corresponds to a quadrupolar distribution (superposition of doublets). Additionally, if we compare the lattice parameters of the pure galaxite, which were obtained for the aged sample, $a = 8.1962 \pm 0.0001$ Å, with that of the galaxite obtained for the wearied sample, $a = 8.1936 \pm 0.0001$ Å, it can be noted that the second is smaller, which may be associated with the substitution of Al by Fe atoms. The Fe atomic size is smaller than that of the Al atom, and is comparable to that of Mn.

It can be observed in Fig. 6 that the spectral area associated with martensite (20.5%) is larger than that for the sample without the wear test, confirming that this phase increases when the sample is submitted to the tribological test. This increase is reflected in the Brinell hardness of the wearied sample, which has a value of 485, larger than that of the aged sample (452).

4 Conclusions

When an as cast Fe-29.0Mn-6Al-0.9C-1.8Mo-1.6Si-0.4Cu (Wt. %) sample was submitted to heat treatment, as shown in Fig. 1, the hardness of the sample increased with the increase in the martensite phase. Furthermore, when this heat-treated sample was submitted to a wear test, additional hardness was obtained due to further increase in the martensite content induced by wear.

Acknowledgements The authors would like to thank the support of Colciencias, Colombian Agency, under contract No. FP44842-032-2016, and the Universidad del Valle.

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