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HARDNESS ANOMALIES ON $Cr_{1-x}Fe_x$ ($0.05<x<0.323$) ALLOYS: MÖSSBAUER EFFECT STUDY

B. TRINDADE[1] and R. VILAR[2]

[1] *Departamento de Engenharia Mecânica, Faculdade de Ciências e Tecnologia da Universidade de Coimbra, 3000 Coimbra, Portugal*

[2] *Departamento de Engenharia de Materiais, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa, Portugal*

The hardness of $Cr_{1-x}Fe_x$ α solid solutions presents an anomalous behaviour in the range 0.10<xFe<0.30, that has been explained either by magnetic or electronic effects. In order to verify wether the anomalies were intrinsic to that phase or were induced by impurities, measurements of microhardness and isomer shift of samples of high purity $Cr_{1-x}Fe_x$ α solid solutions (0.05<xFe<0.323) were carried out. We found that the hardness presents a maximum and a minimum for xFe=0.19 and xFe=0.17, respectively, which are inferior to the amplitudes of the anomalies found by previous authors using lower purity alloys. Within the limit of experimental error, the isomer shift at room temperature varies linearly with the composition. These results suggest that impurities play a major role in determining the magnitude of the hardness anomalies and that electron transfer varies smoothly in the concentration range studied.

1. INTRODUCTION

In previous work /1,2/, it was shown that the hardness of iron-chromium body centered cubic solid solutions presents two relative minima for xFe=0.15 and xFe=0.97 /1,2/. Using Mössbauer spectroscopy, Sauer et al /1/ showed that the minimum of hardness in xFe=0.97 is accompanied by a relative maximum of the isomer shift. Since this maximum is observed for iron atoms with either 0,1 or 2 chromium neighbours in the first two coordination shells, they concluded that the deviation of the isomer shift is caused by a long range transfer of 4s electrons from iron to chromium, which is accompanied by a weakening of the metallic bond and, hence, by a decrease of the hardness of the material. For higher contents of chromium, short range effects become dominant, and the isomer shift decreases linearly with the chromium content. The second anomaly, first observed by Stone /2/, consists on several localised oscillations of the hardness, in the composition range 0.10<xFe<0.30, and a relative minimum around xFe=0.15. The author claims that this behaviour is due to electronic effects, without elucidating the origin and the nature of such effects and their relationship with the hardness anomalies. Electronic effects had already been used to explain the anomalous behaviour of other physical properties in chromium-iron alloys /3,4/. However, it is now believed that, the origin of the majority of these anomalies is magnetic. In particular, iron-chromium alloys exhibit a complex magnetic behaviour for 0.16<xFe<0.19 /5/, which coincides with the composition range where the hardness anomalies were observed.

Previous measurements in paramagnetic iron-chromium alloys /6 to 9/ suggest a linear dependence of the isomer shift on the composition. Besides, the results of positron annihilation and Mössbauer spectroscopy studies, carried out by Szuszkiewicz et al /10/, have shown that there is a net electron transfer from iron to chromium in the concentration range referred above and strongly suggest that electron transfer varies linearly with the composition. These results are in contradiction with what one would expect if the assumptions advanced by Stone /2/, to account for the hardness anomalies, were valid. However, since none of those authors performed a systematic study of carefully prepared Fe-Cr alloys in the composition range where Stone observed the hardness anomalies, the problem is not yet clarified.

In the present work, we present results of a study of microhardness and isomer shift of high purity iron-chromium alloys, in the composition range 0.05<xFe<0.323, using a Vickers indenter and a Mössbauer spectrometer . With our work we intend to clarify the relationship between the microhardness anomalies and the electron transfer.

2. EXPERIMENTAL DETAILS

The samples used in the present work were prepared from multiple pass zone-melted pure metals, melted under argon in a high-vacuum induction furnace. The alloys were degassed in high vacuum before casting. The chemical compositions of the samples, nominal and estimated by an electron microprobe, are indicated in Table I.

Table I
Iron compositions of the alloys, xFe

Alloy	1	2	3	4	5	6
Nominal	0.30	0.18	0.16	0.14	0.10	0.05
Estimated	0.323	0.192	0.167	0.145	0.115	0.05

The samples were mounted, polished and their microhardness measured with a Vickers indenter, under a load of 50g. Each hardness value is the mean of 10 measurements. The Mössbauer absorbers were prepared from metallic powders, obtained by filing the ingots with a diamond file. The Mössbauer spectra were obtained at room temperature, using a transmission configuration. The spectra were fitted to a lorentzian curve using a non-linear least-square computer code, after calibration with respect to the spectrum of a α iron thin foil.

3. RESULTS AND DISCUSSION

The variation of the hardness as a function of the iron content is shown in Fig. 1 and is similar to that presented by Stone /2/; in particular, a minimum of hardness was detected for xFe=0.167. However, both the values of the hardness and of the amplitude of its anomalies that were observed are lower than those observed by Stone /2/. Furthermore, our results put in evidence a minimum of hardness at xFe=0.167 while in Stone' work that is found at xFe=0.15.

Fig. 2 shows the room temperature Mössbauer spectrum of a $Cr_{0.95}Fe_{0.05}$ alloy, with the experimental data fitted with a lorentzian profile, as an example of the spectra recorded from all our samples. The variation of the isomer shift in our alloys versus the iron composition is illustrated in Fig.3. In the same figure we show results of Vilar /6/, Solomon and Levinson /7/, Kuwano and Murooka /8/ and Bansal et al /9/, for comparison with the ones we obtained. One can clearly concluded that, within the limits of the experimental error, the room temperature isomer shift increases linearly with the iron content within the composition range considered, as was expected from previous studies /6 to 9/. The equation I.S.=0.1xFe-0.142 is the best fit to our experimental data.

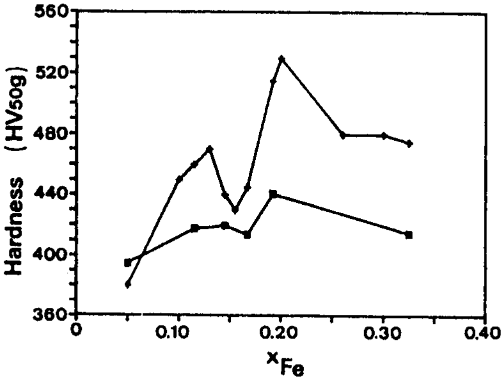

Figure 1. Hardness as a function of Fe content

▪ Our work ◆ H. Stone

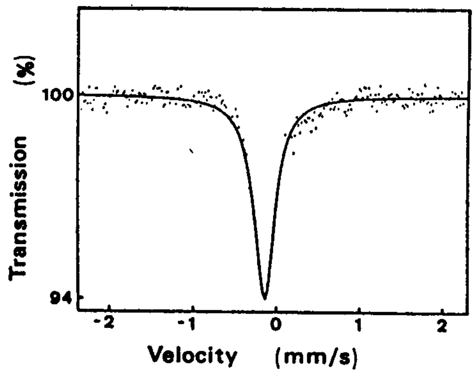

Figure 2. Room temperature spectrum for the Cr0.95Fe0.05 alloy.

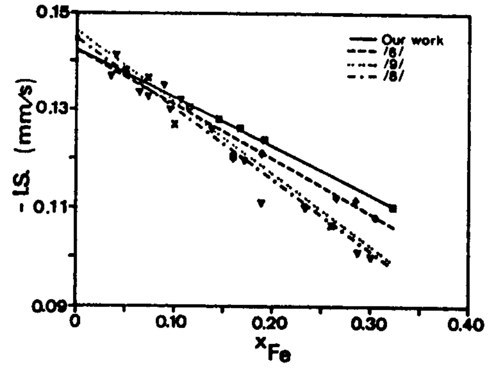

Figure 3. Isomer shift as a function of iron content.

□ Our work + Vilar /6/ ◆ Solomon et al /7/
▾ Kuwano et al /8/ × Bansal et al /9/

The values of isomer shift presented agree, within the limit of experimental error, with those published by Vilar /6/ and Solomon et al /7/, but are slightly inferior to the ones obtained by Kuwano and Murooka /8/ and Bansal et al /9/. This discrepancy might be explained by the fact that the values of the chemical composition of the alloys presented by those authors are most likely nominal; since the vapour tension of chromium is higher than that of iron, there is a very sensible preferential vaporisation of chromium during the samples preparation that cannot be taken into account if nominal compositions are used to convey the experimental results. The same argument may be used to justify the discrepancy between the values of the composition corresponding to the minimum of the hardness we found ($x_{Fe}=0.167$) and that given by Stone /2/ ($x_{Fe}=0.15$). Moreover, the lower values of hardness obtained in the present work are probably explained by the higher purity of the alloys we used, as follows naturally if one considers the purity of the raw materials and the techniques that were used to prepare the alloys in the two works.

The present results confirm that the charge transfer varies smoothly with the iron content in the range where the hardness anomalies appear, in agreement with the conclusions of Szuszkiewicz et al. /10/. Hence, it can be conjectured that the hardness anomalies are not due to electronic effects. On the contrary, it is suggested that they are due to magnetic effects, associated with the transition from antiferromagnetism to ferromagnetism, and with the appearance of a spin-glass type behaviour at low temperature /5/. In addition, it is demonstrated that impurities play a major role in determining the intensity of the hardness anomalies, probably by interstitial-substitutional interaction and atomic clustering, associated with the Fe-Cr metastable miscibility gap.

4. CONCLUSIONS

1. High-purity Fe-Cr alpha solid solutions exhibit hardness anomalies in the composition range $0.10<x_{Fe}<0.30$.
2. The presence of impurities enhance these anomalies.
3. Within the limits of experimental errors, the isomer shift varies linearly with the composition, suggesting that the origin of the hardness anomalies is not electronic.

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