MÖSSBAUER STUDY OF ODS STEELS

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1. Introduction

The paper is focused on MS analyses of oxide dispersion strengthened (ODS) steels from MS characterization point of view.

While ODS steels are complex systems with various elements as an additive, from mössbauer spectroscopy point of view, the iron bearing compounds of the steels, which are in detection limits of the method (>1%), can be reduced to similar system as in dillute Fe-Cr binary alloy.

Dilute iron alloys Fe-X, where X is a 3d transition element, are intensively studied for last 40 years using Mössbauer spectrometry [1]. Hyperfine magnetic fields (B_{hf}) and isomer shifts (IS) at ^{57}Fe nuclei, are used for investigation of the changes in phase composition caused by X element in alloy structure by various authors [2-5].

Changes in parameters of Mössbauer spectra in dilute alloys are assigned mainly to local interactions of atoms. Flinn and Ruby [6] noted that satellite lines in spectra of the Fe–Al system could be described as the superposition of number of sextets for Fe atoms with a different number of Al atoms in the nearest neighborhood, where number of sextets is defined by binomial distribution. Later, this method was extended to other Fe-based alloys. Nowadays such a phenomenological model is generally accepted [7].

2. Experimental details

The investigated ODS steels with different content of chromium were received from laboratories involved in the CRP –ODS project - India (IGCAR), Russia (Bochvar Institute), and Japan (Kyoto University).

The samples for mössbauer experiments were prepared by scrapping into powder form and were measured at room temperature using constant-acceleration Wissel mössbauer spectrometer with the 57Co(Rh) source in transmission geometry. The isomer shifts were determined relative to natural iron. Hyperfine parameters of the spectra including spectral area (Arel), isomer shift (IS), as well as hyperfine magnetic field (Bhf), were refined using the CONFIT fitting software [8], the accuracy in their determination are of ±1 % for relative area, ±0.04 mm/s for isomer shift and ±0.5 T for hyperfine field correspondingly.

3. Results

Sample from India

Pre-alloyed powders of the steel and nano size Y_2O_3 particles were processed in a high energy simoloyer type of mill in argon atmosphere. The mixed powder was canned in mild steel cans, degassed and sealed. The sealed cans were upset to compact the powder into canned billets. The upset billets were machined to remove the mild steel can material. The billets were

hot extruded to produce rods. Mother tubes were prepared by drilling the extruded rods with minimum concentricity. Cladding tubes were produced by multi- stage pilgering of the mother tubes with intermediate softening heat-treatments, and were finally subjected to normalizing and tempering finishing heat treatments in inert atmosphere. The chemical composition of the finished tubes (wt.%) can be seen in table 1.

Tab. 1. Chemical composition of sample from India

Element	C	Cr	W	Ti	Y_2O_3	N	Ni	Si	P	S	O	Mn
wt. %	0.12	8.8	2.01	0.22	0.38	0.0260	<0.02	<0.1	0.004	0.002		0.02

The Mössbauer spectrum of the 9Cr-ODS steel is shown in Fig. 1, its MS parameters are given in Table 2. The spectrum contain sextet of narrow lines, which practically does not differ from that of pure bcc Fe. Besides that, broad, asymmetrical magnetic feature can be seen, as well as minor paramagnetic component in the middle of the spectrum.

Using CONFIT fitting software [8], magnetic part of the spectrum can be decomposed into three components, the hyperfine field of one of which is close to that of pure Fe ($B_{hf0} \approx 34$ T) and the mean values of two others are lower ($B_{hf1} \approx 31$ T, $B_{hf2} \approx 29$ T) (Table 1.). Similar fitting model was used by Petrov *et. al* [4]. The sextet with hyperfine field of one of which is close to that of pure bcc α-Fe (33 T) can be described as iron rich α-phase with almost no Cr impurity in bcc lattice. Two other sextets with hyperfine distribution can be assigned to bcc iron with gradually increased Cr content in the matrix depending on decreasing mean hypefine field value (B_{hf}). Minor paramagnetic singlet in the middle of the spectrum can be described as chromium rich bcc α' phase. Relative areas of spectral components can be used for relative quantification of phase composition. Based on the results, the iron rich α-phase, bcc iron with gradually increased Cr content and chromium rich α' phase forms 19%, 80% and 1%, respectively.
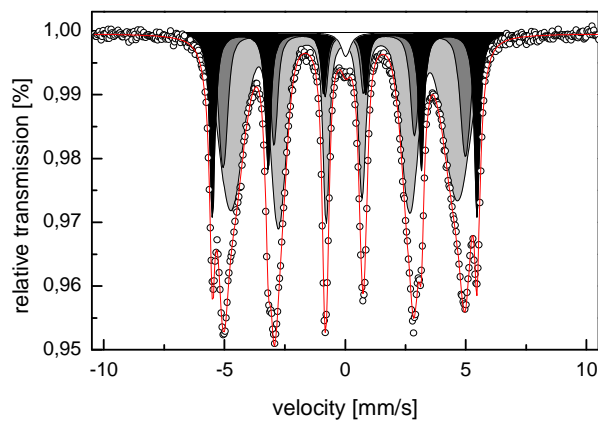

Fig.1. MS spectrum of sample from India. Black component represents bcc Fe, dark grey component represents bcc Fe with few Cr substitutions in the lattice, light grey component represents bcc Fe with more Cr substitutions than in the previous component. White component represents bcc Cr rich phase with few Fe substitutions.

Tab. 2. MS spectral parameters of sample from India

Component	A_{rel} [%]	IS [mm/s]	B_{hf} [T]	B_{dist} [T]	Γ [mm/s]
α	19	-0,02	34,1		0,27
Fe-Cr	20	-0,04	31,2	1,9	0,28
Fe-Cr	60	-0,04	29,2	6,9	0,24
α'	1	0,02			0,47

Sample from Russia (EP 450)

The chemical composition of sample EP 450 can be seen in table 3.

Tab. 3. Chemical composition of sample EP 450.

Element	Cr	C	Si	Mn	Mo	Ni	B	V	Nb
wt.%	11-13.5	0.1	1	1	3.7	0.05-0.3	0.015	0.1-0.3	0.15-0.4

The Mössbauer spectrum of sample EP 450 is shown in Fig. 2, its parameters are given in Table 4. The spectrum contain sextet of narrow lines, which practically does not differ from that of pure bcc Fe. Besides that, broad, asymmetrical magnetic feature can be seen, as well as minor paramagnetic component in the middle of the spectrum.
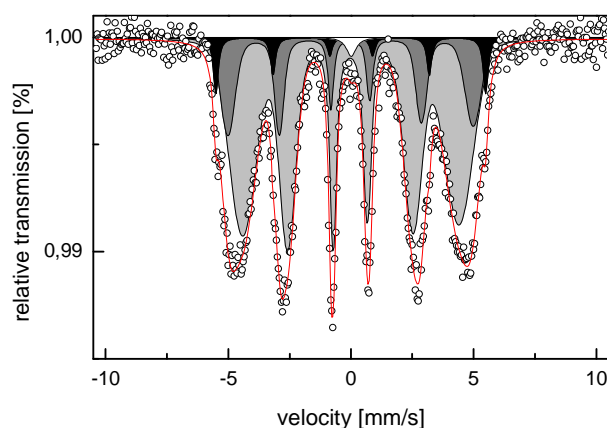

Fig.2. MS spectrum of sample EP 450. Black component represents bcc Fe, dark grey component represents bcc Fe with few Cr substitutions in the lattice, light grey component represents bcc Fe with more Cr substitutions than in the previous component. White component represents bcc Cr rich phase with few Fe substitutions.

Magnetic part of the spectrum can be decomposed into three components, the hyperfine field of one of which is close to that of pure Fe ($B_{hf0} \approx 34$ T) and the mean values of two others are lower ($B_{hf1} \approx 31$ T, $B_{hf2} \approx 27$ T) (Table 4.). The sextet with hyperfine field of one of which is close to that of pure bcc α-Fe (33 T) can be described as iron rich α-phase with almost no Cr impurity in bcc lattice. Two other sextets with hyperfine distribution can be assigned to bcc iron with gradually increased Cr content in the matrix depending on decreasing mean hypefine field value (B_{hf}). Minor paramagnetic singlet in the middle of the spectrum can be described as chromium rich bcc α' phase. Relative areas of spectral components can be used for relative quantification of phase composition. Based on the results, the iron rich α-phase, bcc iron with gradually increased Cr content and chromium rich α' phase forms 5%, 94% and 1%, respectively.

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Tab. 4. MS spectral parameters of sample EP 450.

Component	A_{rel} [%]	IS [mm/s]	B_{hf} [T]	B_{dist} [T]	Γ [mm/s]
α	5	0.00	34.2		0.24
Fe-Cr	21	-0.02	31.1	3.8	0.24
Fe-Cr	73	-0.02	27.4	7.6	0.25
α'	1	0.01			0.48

Sample from Japan (KOT 19)

The chemical composition of samples KOT 19 can be seen in table 5.

Tab. 5. Chemical composition of sample from Japan.

	C	Si	Mn	Cr	W	Al	Ti	Y	O	Y2O3	Ex.O
KOT-19	0.045	0.03	0.03	13.6	1.9	0.02	0.16	0.26	0.11	0.33	0.04

The Mössbauer spectrum of sample KOT 19 is shown in Fig. 3, its parameters are given in Table 6. The spectrum contain sextet of narrow lines, which practically does not differ from that of pure bcc Fe. Besides that, broad, asymmetrical magnetic feature can be seen, as well as minor paramagnetic component in the middle of the spectrum.

Magnetic part of the spectrum can be decomposed into three components, the hyperfine field of one of which is close to that of pure Fe ($B_{hf0} \approx 34$ T) and the mean values of two others are lower ($B_{hf1} \approx 30$ T, $B_{hf2} \approx 27$ T) (Table 6.). The sextet with hyperfine field of one of which is close to that of pure bcc α-Fe (33 T) can be described as iron rich α-phase with almost no Cr impurity in bcc lattice. Two other sextets with hyperfine distribution can be assigned to bcc iron with gradually increased Cr content in the matrix depending on decreasing mean hyperfine field value (B_{hf}). Minor paramagnetic singlet in the middle of the spectrum can be described as chromium rich bcc α' phase. Relative areas of spectral components can be used for relative quantification of phase composition. Based on the results, the iron rich α-phase, bcc iron with gradually increased Cr content and chromium rich α' phase forms 4%, 95% and 1%, respectively.
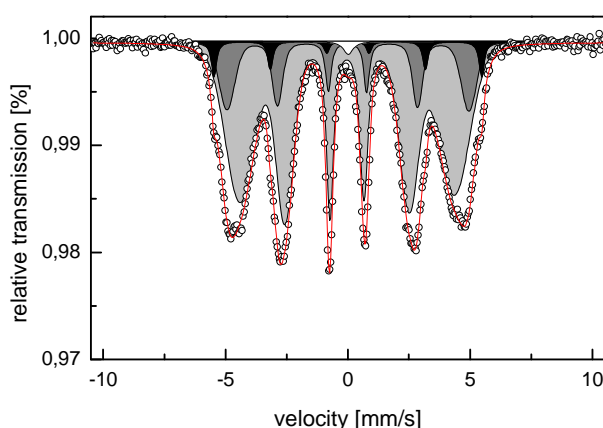

Fig.3. MS spectrum of sample KOT 19. Black component represents bcc Fe, dark grey component represents bcc Fe with few Cr substitutions in the lattice, light grey component represents bcc Fe with more Cr substitutions than in the previous component. White component represents bcc Cr rich phase with few Fe substitutions.

Tab. 6. MS spectral parameters of sample KOT 19

Component	A_{rel} [%]	IS [mm/s]	B_{hf} [T]	B_{dist} [T]	Γ [mm/s]
α	4	0.00	34.0		0.25
Fe-Cr	18	0.00	30.7	3.8	0.24
Fe-Cr	77	-0.03	27.3	8.2	0.26
α'	1	0.02			0.48

4. Conclusion

All of the ferritic samples measured by MS spectrometry featured similar components in the iron bearing phases of the analyzed steels. Based on Cr content, relative areas of individual spectral components differ, as well as mean hyperfine field of Fe-Cr components, but it seems that chosen fitting model describes all samples well.

Chosen fitting model is consists of pure bcc α-Fe, bcc Fe with Cr substitution and paramagnetic bcc Cr rich component. All of these features can be seen in samples from India, Russia as well as in two of the samples from Japan.

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