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Magnetic measurements of the reverse martensite to austenite transformation in a rolled austenitic stainless steel

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The reverse (α'-γ) transformation in 304 stainless steel (SS) has been studied by magnetic measurements. Specimens rolled 15 to 55% reduction in thickness were annealed at various temperatures and times. After annealing at temperatures between 300–600°C for 5 min the saturation magnetization values increased when compared to the saturation magnetization values after rolling. Specimens rolled to 40 to 55% reduction after annealing at 500°C showed the highest saturation magnetization. Saturation magnetization sharply decreases at annealing temperature above 625°C which indicates the start of reverse (α'-γ) transformation. The decrease in saturation magnetization is rapid for annealing time from 5 to 40 min, whereas, the decrease in saturation magnetization is relatively low for annealing time above 40 min. The hardness values after reverse (α'-γ) transformation at temperatures between 300–600°C is slightly greater attributed to the increase in α' martensite and above this temperature the hardness dropped substantially as a result of recovery and recrystallization. The results show that there is a decrease in coercive force at temperatures between 300–500°C and may be due to an increase in α' martensite phase. A further decrease in coercive force at temperature between 500 and 625°C may be attributed to the sweeping out of some dislocation from the martensite phase. This is followed by a sharp increase in coercive force at temperature up to 800°C and is attributed to a shape magnetic anisotropy effect. At temperatures between 800–900°C a rapid decreased in coercive force occurs. At temperatures between 900–1100°C the decrease in coercive force is not so sharp dominant. The decrease in coercive force above 800°C corresponds to softening of the stainless steel due to recrystallization. From the changes in the values of saturation magnetization the A_s temperature is estimated to be between 625–650°C, and the A_f to be between 900–950°C. © *2004 Kluwer Academic Publishers*

1. Introduction

One of the urgent problems of technological safety is forecasting the service life of structural materials. The structural performance of steels are limited due to the accumulation of stresses during service as result of prolonged exposure to mechanical and thermal loads, as well as aggressive environments. Under the impact of these factors both the internal structure of the material and its mechanical and magnetic properties are changed [1].

Martensitic transformation in stainless steel is unwanted because it results in loss of ductility. The combination of mechanically and/or thermally induced stresses are responsible for martensitic transformation. It is already known that Type 304 stainless steel, which is non-magnetic at room temperature, becomes ferromagnetic after it is cold-worked or subjected to subzero treatments, as a result of martensitic transformation from facecentered cubic γ to body-centered cubic α' lattice [2–9].

In stainless steel, the dislocations and twins are considered to be the major sources for martensitic phase transformation that is formed upon undergoing a plastic deformation or subzero treatments and hence its secular degradation [10–16]. Therefore, the presence of martensitic phase in these stainless steels can introduce several disadvantages regarding their metallurgical stability, particularly with temperature and strain excursion after formation.

To improve the mechanical properties of stainless steel, it is therefore important to study the reheating behavior of such α' martensitic transformed stainless steels. The reverse (α'-γ) transformation is significant in relation to the behavior of certain stainless steels used in reactor applications [17]. Reverse (α'-γ) transformation of partially martensitic structures in stainless

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TABLE I Chemical composition of the 304 stainless steel

Element	C	Cr	Ni	Mn	Si	P	S	Fe
Content (wt %)	0.06	18.44	8.33	1.16	0.43	0.033	0.009	Bal.

steels provides a potential means of improving the mechanical properties of austenite through the production of fine-grained structures [18]. Moreover, the annealing out of the defects in martensitic structures at, or above, the austenitizing temperature is an important aspect of strengthening stainless steels by reversion [19]. Therefore, the distribution and percentage of martensitic phase and its reversion can be altered through proper selection of heat treatment temperature and time. There is relatively little information available on the α' martensite to γ austenite reversion that occurs when such stainless steels are heated rapidly.

As magnetic properties are highly sensitive to the structure of materials, magnetic properties of the stainless steel change due to reversion of α' martensite to γ austenite phase. Therefore, in this study the reverse (α'-γ) transformation of cold rolled specimens after annealing at various temperatures and times have been investigated by means of magnetic measurements. It is also possible to determine the starting (A_s) and final (A_f) temperatures of reversion for stainless steel.

2. Experimental procedure

Type 304 austenitic stainless steel was used in this investigation. Samples were received as 100 mm length × 50 mm width × 1.85 mm thick hot-rolled plate stock. The chemical composition is shown in Table I. The microstructure of the as received material is shown in Fig. 1. The average grains size as determined by intercept method is 25 μm. The grain structure is essentially austenitic, containing a negligible volume percent of α' martensite as determined by magnetic measurement.

Specimens for room temperature (25°C) rolling were prepared from the rolled plate parallel to the rolling direction by a Spark wire cutting machine (Fine Sodick Wire Cut EDM). Rectangular strips, 100 mm length × 12 mm width × 1.85 mm thickness were used for rolling. The specimens were subjected to cold rolling to achieve 15, 20, 25, 30, 35, 40, 45 and 55% reductions in thickness. The plastic strain rates were assumed to be essentially constant in all the cases. At least three specimens were cold rolled at room temperature for each measurement. Details of the rolling reduction and experimental techniques have been reported previously [20].

After rolling, all specimens were cut by a spark wire cutting machine into size of 3.5 mm × 3 mm so as to maintain the rolling direction and to obtain our experimental data. All specimens were electro-polished using a 170 ml:30 ml solution of ethanol and perchloric acid at 30 V for 45 s prior to reverse (α'-γ) transformation and magnetic measurements.

The reverse (α'-γ) transformation was obtained by heating the specimens in an Image Furnace ULVAC MILA–3000 that had a temperature accuracy of ±1°C. To accomplish the reverse (α'-γ) transformation, the specimens were rapidly heated to an annealed temperature and held for specified times then followed by a water quench to room temperature (25°C).

The specimens for reversion treatments are of two types. In the first set, specimens with different percent of rolling reduction in thickness are annealed at temperature ranging from 300 to 800°C at the increment of 100°C for 5 min. Moreover, specimens rolled to 55% reduction are also annealed at temperatures between 300 to 1100°C for 5 min. In the second set, specimens rolled to 55% reduction are annealed at temperature ranging from 600 to 700°C at the increment of 25°C for 5, 10, 20, 40, 80, 120 and 320 min. After the heat treatment, all specimens were again electro-polished as described earlier prior to the magnetic measurements.

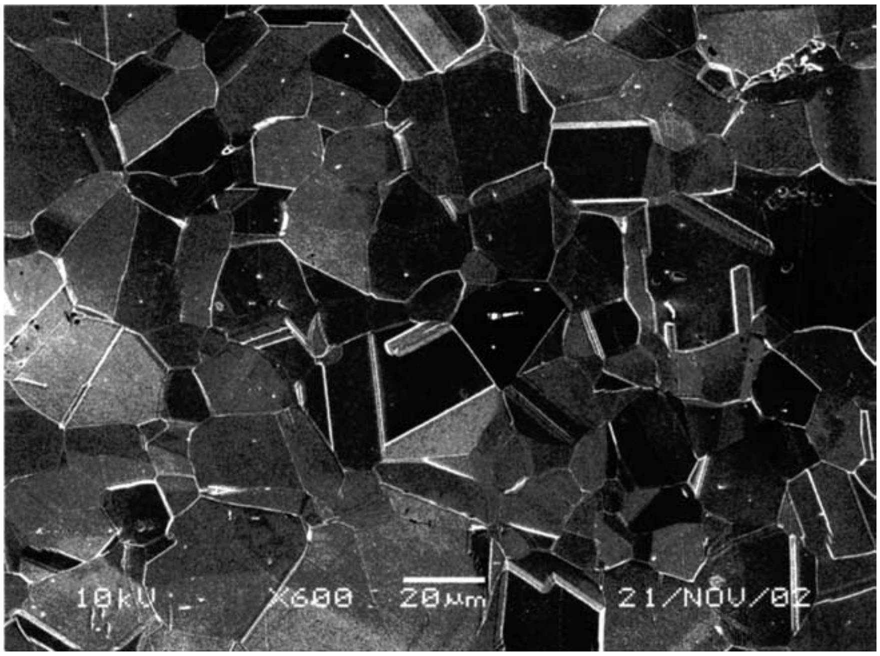


Figure 1 SEM micrograph of as received 304 austenitic stainless steel.

The specimens are subsequently used for magnetic measurements and scanning electron microscopy (SEM). The saturation magnetization (M_s) values are obtained from magnetization curves using a superconducting quantum interference device (SQUID) Design MPMS XL magnetometer at room temperature in applied field of 0 to 30 kOe. The values of coercive force (H_c) are obtained from magnetic hysteresis loops with a vibrating sample magnetometer (VSM) at room temperature in the applied magnetic field of -20 to $+20$ kOe. The values of saturation magnetization are also obtained by VSM for the comparison of two magnetometers used in this study. Hardness (HV) measurements are used to complement the magnetic measurements after reverse (α'-γ) transformation. Micro-hardness testing is done on the specimens with a mirror-like surface finish obtained by electropolishing, using Akashi MVK-FII hardness tester. The microstructures are characterized using Jeol JSM-5510 electron microscope (SEM). For SEM examination a mixture of nitric acid and hydrochloric acid (1:3) solution is used to etch the specimens. TEM specimens were prepared parallel to the surface (planar section) of the specimens. Thin foils were prepared by polishing to approximately 80 μm. Subsequent thinning was carried out by twin jet electro-polishing in a solution of perchloric acid and acetic acid (volume ratio was 1:9) at the voltage of 40–45 V at room temperature.

3. Results

3.1. The direct martensite transformation

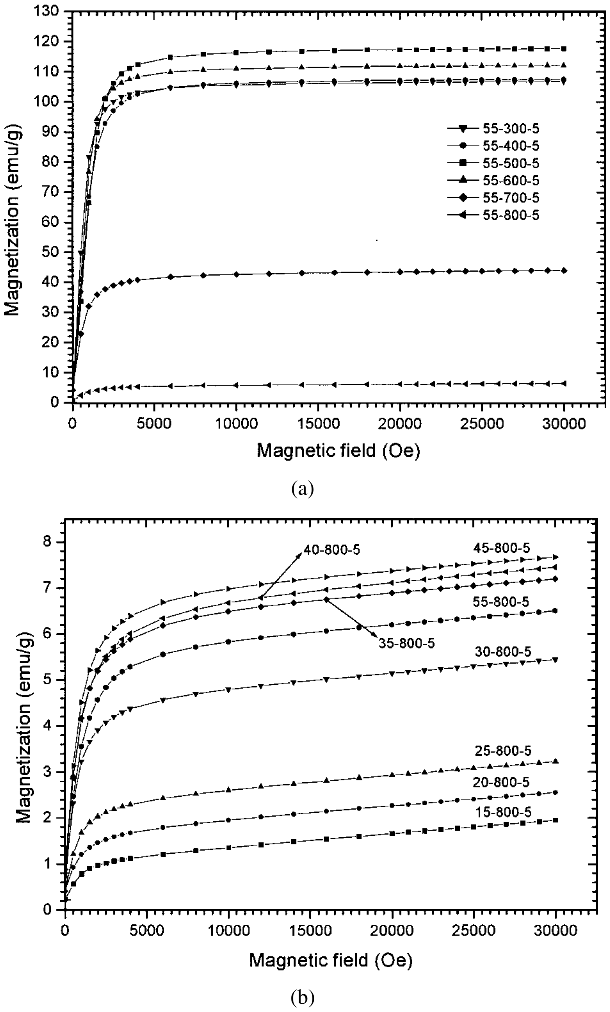
Cold rolling at room temperature from 15 to 55% reduction produced 5 to 74% ferromagnetic α' martensite phase [20]. The saturation magnetization showed a remarkable increase with the increased percent of reduction in thickness. The value of saturation magnetization after 55% reduction is 104 emu/g, corresponding to about 74 vol% ferromagnetic phase [20]. The coercive force varied inversely from the saturation magnetization with the increased percent of reduction in thickness. Coercive force is found to decrease with the increased percent of reduction, and is a function of the distribution and volume percent of the α' martensite phase. Stainless steel specimens after cold rolling of 15 to 55% reduction showed different shapes of α' martensite [20]. Specimens rolled to 55% reduction in thickness formed irregular block shaped α' martensite with an increase in dislocation density, as shown in Fig. 2 The influence of rolling reduction on the austenite to martensite transformation and its magnetic measurements are discussed in a preceding paper [20].

Figure 2 TEM micrograph and selected area diffraction pattern of austenitic stainless steel rolled to 55% reduction in thickness.

3.2. Magnetization versus magnetic field

The magnetization versus magnetic field curves of Fig. 3a and b demonstrate the effect of annealing temperature and reduction percent in thickness respectively. The curves are obtained by SQUID magnetometer. Fig. 3a shows the magnetization curves for the specimens cold rolled to 55% reduction in thickness and subsequently annealed at temperatures between 300 to 800°C for 5 min. As compared to the specimen annealed at 300°C for 5 min, annealing at 800°C for 5 min decreases the magnetization. A small amount of ferromagnetic phase exist in the specimen annealed at 800°C for 5 min. However, there is little difference between the magnetization values of the specimens annealed at temperatures between 300 and 600°C (Fig. 3a). The magnetization curve for specimen annealed at 500°C for 5 min shows the highest magnetization, even higher than the specimen cold rolled to 55% reduction in thickness. The magnetization curve obtained for a specimen annealed at 1100°C for 5 min is comparable to the as received specimen (Figure not shown here) [20].

Fig. 3b shows the magnetization curves for the specimens cold rolled to 15 to 55% reduction in thickness after annealing at 800°C for 5 min. Annealing at temperature 800°C for 5 min shows that magnetization of the specimens depends on the amount of plastic deformation and increases with the increased percent of rolling reduction. And magnetization curve for specimen with 55% reduction in thickness annealed at 800°C for 5 min lies between the curves of the specimens cold rolled to 30 and 35% reduction in thickness, showing decrease in magnetization.



(a)

(b)

Figure 3 Magnetization plotted against magnetic field measured by SQUID. (a) rolled to 55% reduction annealed at 300–800°C for 5 min and (b) rolled to 15–55% reduction annealed at 800°C for 5 min.

3.3. Saturation magnetization

Varying amount of ferromagnetic martensite phase was introduced in austenitic stainless steel by room temperature rolling and subsequently reverted by annealing at different temperatures and times. The saturation magnetization and amount of martensite after reversion treatment were quantified by VSM. Saturation magnetization is proportional to the volume of ferromagnetic phase, and in austenitic stainless steel, of the two phases, γ austenite and α' martensite that can coexist, α' martensite is the only ferromagnetic phase. The value of saturation magnetization, 154 emu/g corresponds to the 100% α' martensite phase [21]. In the as received state, the saturation magnetization of stainless steel at room temperature (25°C) is about 0.55 emu/g, therefore, in the specimen about 0.36% α' martensite phase is induced. Table II shows the magnetic properties, hardness, volume percent of α' martensite, and reversed γ austenite of stainless steel after rolling and subsequent annealing at various temperatures and times.

Fig. 4 shows saturation magnetization as a function of temperature for specimens that are cold rolled to 15 to 55% reduction in thickness and annealed for 5 min. Results show the coexistence of ferromagnetic and paramagnetic phases depending on the percent of reduction in thickness, annealing temperature and time. The saturation magnetization values for specimens cold rolled to 15 to 55% reduction in thickness after annealing at temperatures between 300 to 600°C are increased as compared to the saturation magnetization values after cold rolling to 15 to 55% reduction in thickness (see Table II). Moreover, the saturation magnetization values for the specimens rolled to 40 to 55% reduction in thickness after reversion at 500°C are higher than the specimens rolled to 15 to 35% reduction. For the specimen rolled to 55% reduction in thickness after

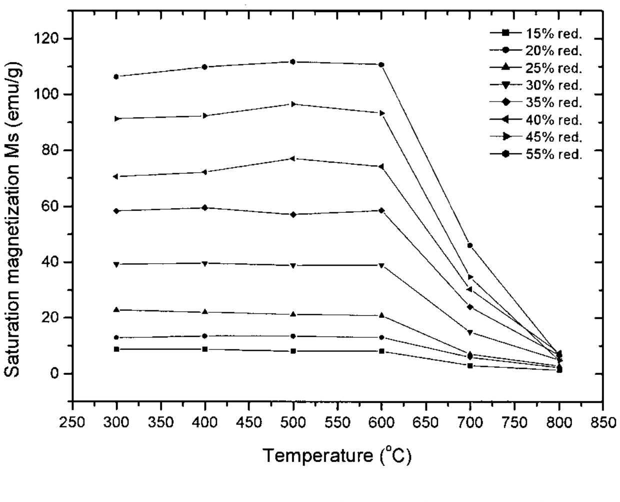


Figure 4 Saturation magnetization as a function of temperature for specimens rolled to 15–55% reduction annealed for 5 min.

TABLE II Magnetic properties, hardness, volume percent of α' martensite and reversed γ austenite of rolled stainless steel after reverse (α'-γ) transformation

No.	Condition	M_s (emu/g)	H_c [X] (Oe)	H_c [Y] (Oe)	H_c [Z] (Oe)	α' (%)	Rev. γ (%)	HV
1	As received	0.55	32.21	32.59	40.00	0.36	–	193
2	15-RT-0	7.76	166.6	189.7	234.9	5.04	–	296
3	15-300-5	8.72	165.0	184.1	234.0	5.66	–	–
4	15-400-5	8.79	156.6	176.4	230.7	5.71	–	–
5	15-500-5	8.16	152.5	169.2	224.0	5.30	–	–
6	15-600-5	8.20	150.5	162.4	223.8	5.32	–	–
7	15-700-5	2.93	274.3	279.0	368.6	1.91	3.13	–
8	15-800-5	1.35	302.4	316.6	390.3	0.88	4.16	–
9	20-RT-0	12.20	137.6	155.7	204.0	7.92	–	325
10	20-300-5	12.85	139.7	155.1	205.1	8.34	–	–
11	20-400-5	13.42	139.5	150.6	204.5	8.71	–	–
12	20-500-5	13.45	134.7	150.9	198.9	8.73	–	–
13	20-600-5	13.06	130.0	140.4	188.8	8.48	–	–
14	20-700-5	3.97	219.1	224.0	299.5	3.88	4.04	–
15	20-800-5	2.22	272.1	280.2	356.4	1.44	6.48	–
16	25-RT-0	20.63	108.2	126.1	180.0	13.39	–	355
17	25-300-5	22.78	106.7	125.6	180.6	14.70	–	–
18	25-400-5	22.04	102.0	119.2	178.9	14.31	–	–
19	25-500-5	21.30	98.40	116.9	175.4	13.83	–	–
20	25-600-5	20.86	92.55	102.8	155.6	13.55	–	–
21	25-700-5	7.04	204.3	209.0	293.0	4.57	8.82	–
22	25-800-5	2.84	252.7	255.3	342.6	1.85	11.55	–
23	30-RT-0	37.66	79.65	94.28	145.2	24.46	–	383
24	30-300-5	39.26	82.18	96.92	149.9	25.49	–	–
25	30-400-5	39.58	81.91	96.09	151.0	25.7	–	–
26	30-500-5	38.92	78.18	91.19	142.1	25.27	–	–
27	30-600-5	38.94	74.85	84.20	129.2	25.29	–	–
28	30-700-5	14.96	172.8	183.5	256.0	9.71	14.75	–
29	30-800-5	4.98	214.3	217.0	305.6	3.23	21.23	–
30	35-RT-0	58.47	65.02	75.34	120.7	37.95	–	407
31	35-300-5	58.28	66.08	76.03	123.7	37.85	–	–
32	35-400-5	59.49	65.24	74.08	120.8	38.63	–	–
33	35-500-5	57.10	63.20	72.66	124.1	37.08	–	–
34	35-600-5	58.54	58.91	65.86	109.6	38.01	–	–
35	35-700-5	23.93	154.6	164.4	246.6	15.54	22.43	–
36	35-800-5	6.71	202.6	210.7	290.9	4.36	33.61	–
37	40-RT-0	73.76	57.00	63.66	100.0	47.9	–	427
38	40-300-5	70.60	58.57	63.92	101.4	45.85	–	–
39	40-400-5	72.22	57.54	62.0	98.23	46.89	–	–
40	40-500-5	77.04	54.10	60.07	95.6	50.02	–	–
41	40-600-5	74.26	51.87	56.29	90.75	48.22	–	–
42	40-700-5	30.26	147.9	157.2	233.0	19.65	28.25	–
43	40-800-5	7.51	198.4	206.1	267.9	4.88	43.02	–
44	45-RT-0	84.49	48.83	52.47	82.07	54.87	–	475
45	45-300-5	91.23	49.23	52.91	82.86	59.24	–	–
46	45-400-5	92.45	48.99	52.65	81.55	60.03	–	–
47	45-500-5	96.52	49.04	52.04	80.36	62.67	–	–
48	45-600-5	93.32	42.92	46.37	74.13	60.6	–	–
49	45-700-5	34.69	148.0	157.4	235.8	22.53	32.34	–
50	45-800-5	7.78	176.4	185.9	248.5	3.10	51.76	–
51	55-RT-0	103.57	48.71	49.51	74.08	67.25	–	485
52	55-300-5	106.40	47.61	48.75	77.98	69.09	–	490
53	55-400-5	109.85	47.09	47.89	74.51	71.33	–	492
54	55-500-5	111.78	47.00	47.32	72.91	72.58	–	492
55	55-600-5	110.79	39.95	41.67	66.75	71.94	–	488
56	55-600-10	102.61	46.71	47.05	75.19	66.63	0.62	–
57	55-600-20	95.26	63.69	65.36	100.7	61.86	5.39	–
58	55-600-40	86.12	82.20	83.06	127.1	55.93	11.32	–
59	55-600-80	78.44	96.07	97.35	148.2	50.93	16.32	–
60	55-600-160	74.08	100.9	104.6	158.4	48.10	19.15	–
61	55-600-320	71.99	101.8	106.6	162.5	46.74	20.15	–
62	55-625-5	104.8	41.05	42.58	67.42	68.09	–	470
63	55-625-10	92.30	61.46	62.31	95.65	59.94	7.31	–
64	55-625-20	78.67	91.78	91.90	142.9	51.08	16.17	–
65	55-625-40	66.33	108.2	113.2	173.4	43.07	24.18	–
66	55-625-80	59.98	111.3	120.4	183.9	38.95	28.30	–
67	55-625-160	57.66	110.6	119.8	180.4	37.44	29.81	–
68	55-625-320	54.68	107.2	117.8	178.6	35.50	31.75	–
69	55-650-5	90.99	51.32	64.20	101.7	59.09	8.16	445
70	55-650-10	69.06	102.1	105.0	157.2	44.84	22.41	–
71	55-650-20	57.41	120.1	128.7	193.2	37.28	29.97	–
72	55-650-40	50.72	122.1	133.4	199.9	32.93	34.32	–
73	55-650-80	47.59	120.0	131.5	196.7	30.90	36.35	–
74	55-650-160	46.14	117.3	130.3	194.1	29.96	37.92	–
75	55-650-320	43.36	115.0	128.0	191.1	28.16	39.09	–
76	55-675-5	68.43	94.76	98.48	157.9	44.44	22.81	420
77	55-675-10	46.26	133.3	144.3	215.6	30.04	37.21	–
78	55-675-20	39.53	136.5	149.6	219.8	25.67	41.58	–
79	55-675-40	33.92	132.4	146.6	213.2	22.03	45.22	–
80	55-675-80	31.77	129.4	143.4	208.5	20.63	46.62	–
81	55-675-160	30.18	127.9	140.7	203.1	19.60	47.65	–
82	55-675-320	27.39	125.8	137.5	198.3	17.79	49.46	–
83	55-700-5	45.99	134.8	144.9	215.1	29.87	37.38	385
84	55-700-10	32.86	145.4	160.5	231.7	21.34	45.91	–
85	55-700-20	30.92	148.5	162.1	234.5	20.08	47.17	–
86	55-700-40	28.64	141.0	155.8	224.6	18.60	48.65	–
87	55-700-80	26.02	138.2	151.9	217.1	16.90	50.35	–
88	55-700-160	24.24	134.6	149.5	211.0	15.74	51.51	–
89	55-700-320	21.03	132.4	145.3	204.7	13.56	53.69	–
90	55-800-5	6.57	163.7	172.5	231.8	4.27	62.98	278
91	55-900-5	0.98	60.53	62.1	88.5	0.63	66.62	209
92	55-1000-5	0.83	57.28	60.24	75.32	0.54	66.71	200
93	55-1100-5	0.64	42.24	49.1	51.43	0.41	66.84	189

Reduction (%)—Temperature (°C)—Time (min), M_s: saturation magnetization, H_c: coercive force, Rev γ: reversed austenite, HV: Hardness.

annealing at 500°C for 5 min, the value of saturation magnetization is 111.78 emu/g, which indicates that the specimens has the highest volume percent of α' martensite (72.58%) as shown in Table II. The differences in magnetic characteristics appear significant and saturation magnetization is sharply decreased at an annealed temperature above 600°C. Results show that the specimens with 15 to 55% reduction in thickness after annealing at 800°C for 5 min has the lowest saturation magnetization. And it is estimated to be about 1.353 and 6.75 emu/g for specimens with 15 and 55% reduction in thickness, respectively. This means that reversion of α' martensitic phase to γ austenitic phase does take place. The specimen cold rolled to 55% reduction is ferromagnetic up to about 600°C (increase in saturation magnetization) and it transforms from α' martensite to reversed γ austenite phase and its saturation magnetization drops abruptly to 0.98 emu/g at 900°C and 0.642 emu/g at 1100°C. The magnetism is paramagnetic at a temperature above 1000°C because values of saturation magnetization are comparable to the saturation magnetization value of the as received specimens.

Results are also plotted to compare the saturation magnetization values obtained by SQUID and VSM magnetometers. Fig. 5 compares the saturation magnetization plotted against percent of reduction in thickness after annealing at 700 and 800°C for 5 min measured by SQUID and VSM. The results show that slightly more variation in the values of saturation magnetization is observed when measured by the SQUID than those calculated by the VSM (Table III).

Fig. 6 shows variation of log M_s with annealing temperature. The specimen rolled to 55% reduction in

TABLE III Comparison between the values of saturation magnetization measured by SQUID and VSM after reverse (α'-γ) transformation

No.	Condition	M_s (emu/g) SQUID	M_s (emu/g) VSM
1	15-700-5	3.06	2.93
2	20-700-5	4.44	3.97
3	25-700-5	7.57	7.04
4	30-700-5	16.24	14.96
5	35-700-5	24.17	23.93
6	40-700-5	28.16	30.26
7	45-700-5	31.69	34.69
8	55-700-5	42.61	45.99
9	15-800-5	1.09	1.35
10	20-800-5	1.69	2.22
11	25-800-5	2.34	2.84
12	30-800-5	4.56	4.98
13	35-800-5	6.29	6.71
14	40-800-5	6.44	7.51
15	45-800-5	6.77	7.78
16	55-800-5	5.59	6.57

Reduction [%]—Temperature (°C) —Time (min), M_S: saturation magnetization.

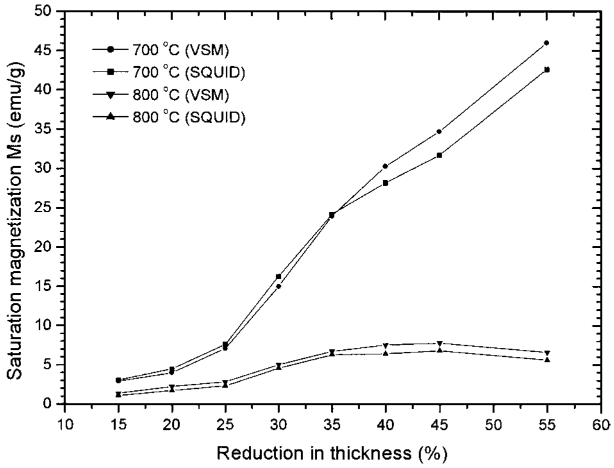


Figure 5 Saturation magnetization plotted against percent reduction in thickness measured by SQUID and VSM magnetometers.

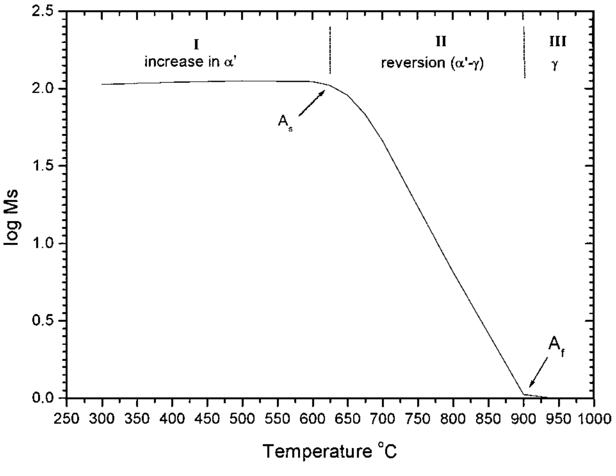


Figure 6 Variation of log M_s with annealing temperature for specimens rolled to 55% reduction annealed for 5 min.

thickness is annealed at temperatures between 300 to 1000°C for 5 min. In the Fig. 6 three different regions of saturation magnetization can be seen. Region I corresponds to the saturation magnetization values at temperatures between 300–625°C. In region I a slight increase in saturation magnetization can be observed. Region II corresponds to sharp decrease in saturation magnetization due to reversion of α' martensite into γ austenite at temperatures above 625°C and up to 900°C. In region III a loss of saturation magnetization at temperatures above 900°C is observed because of nearly complete α' martensite reversion due to recrystallization. Therefore, by using magnetic property we may estimate A_s and A_f temperatures. The A_s signifies the temperature at which the martensite start to transform to austenite, while A_f is the temperature above which austenite transformation was complete. The A_s and A_f temperatures may be calculated from Fig. 6. In reverse (α'-γ) transformation (Fig. 6), A_s is the temperature where the curve of region I deviates or where the region II starts. And A_f may be the point where region II ends. Therefore, A_s and A_f temperatures of reversed stainless steel used in this study are between 625–650°C and between 900–950°C, respectively. Annealing at temperature 650°C for 5 min resulted in decrease of saturation magnetization. This indicates that the reversion of α' martensite to γ austenite may progress at this temperature even for a short annealing time of 5 min. However, annealing at temperatures between 300 and 625°C for 5 min increased the saturation magnetization as compared to the cold rolled specimen with 55% reduction in thickness (Table II).

In order to see the effect of longer-time annealing on saturation magnetization, the specimens were annealed at temperatures between 600 and 700°C from 5 to 320 min. Fig. 7 shows saturation magnetization as a function of annealing time for specimens rolled to 55% reduction in thickness annealed at temperatures between 600 and 700°C. Results show that the saturation magnetization of stainless steel varied with annealing time and temperature. It was observed that the specimen annealed at temperature 700°C for 320 min has the lowest value of saturation magnetization (21.03 emu/g) and volume of α' martensite (13.56%), while the specimen annealed at temperature 600°C for 320 min has the higher value of saturation magnetization (71.99 emu/g) and volume of α' martensite (46.74%). Results also show that the specimens annealed for 10 min at temperatures between 600 and 625°C decreased the saturation

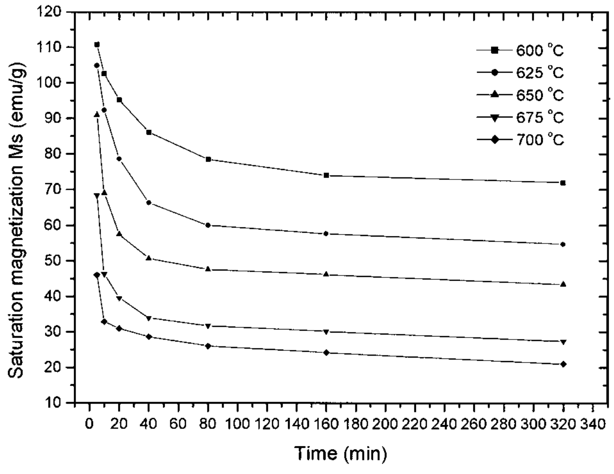


Figure 7 Saturation magnetization as a function annealing time for specimens rolled to 55% reduction and annealed at 600 to 700°C.

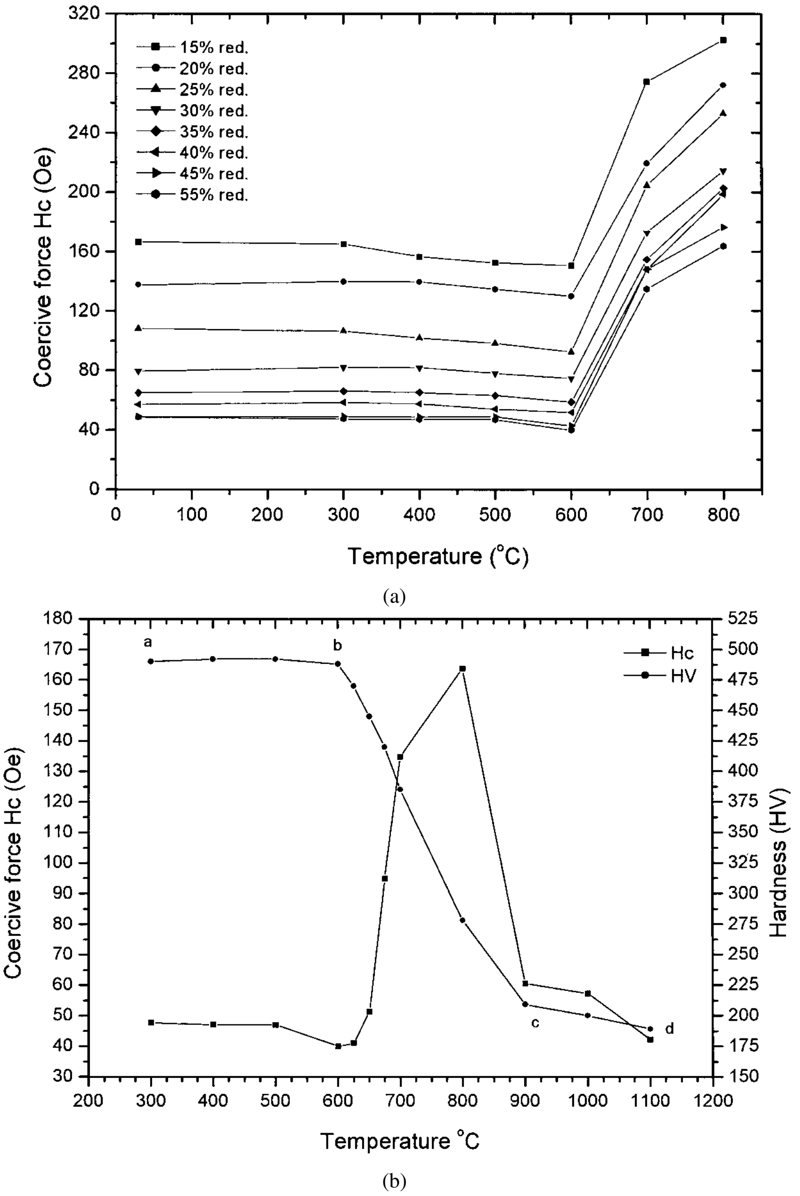
magnetization, indicating that reversion of α' martensite to γ austenite has also started which is not observed after annealing for 5 min (Table II).

Moreover, the decrease in saturation magnetization is sharp for annealing time from 5 to 40 min, whereas, the decrease in saturation magnetization is relatively low for annealing time above 40 min. The decrease in saturation magnetization accounts for the decrease in volume percent of α' martensite.

3.4. Coercive force

The coercive force is derived from magnetic hysteresis loop measurements performed with a VSM magnetometer. Fig. 8a and b show the coercive force plotted against annealing temperature for the specimens cold rolled to 15 to 55% reduction in thickness. Fig. 8a shows the coercive force after annealing at different temperatures for 5 min. Coercive force decreases with the increase in annealing temperature up to 600°C, and above 600°C coercive force increased sharply in all the specimens cold rolled to 15 to 55% reduction in thickness. Results also show that the values of coercive force are slightly higher at room temperature than after annealing at 300°C.

Fig. 8b shows the coercive force for specimen with 55% reduction in thickness after annealing at different temperatures for 5 min. The coercive force is also measured at temperatures between 600 and 700°C with the increment of 25°C (Fig. 8b). As shown in Fig. 8b the decrease in coercive force is observed up to 625°C and then a sharp increase in coercive force up to 800°C. The value of coercive force (163.7 Oe) is highest at an annealing temperature of 800°C. At temperatures above 800°C the coercive force decreases sharply until it reaches an annealing temperature of 900°C. Results also show that at temperatures above 900°C it decrease with increasing temperature, and at 1100°C the value of coercive force is 42.24 Oe lower than the value of coercive force at 300°C (47.61 Oe), and higher than the value of coercive force of as received specimen (32.21 Oe).



(a)

(b)

Figure 8 (a) Coercive force as a function of temperature for specimens rolled 15 to 55% reduction and annealed for 5 min and (b) Coercive force and hardness plotted against temperature for specimens rolled to 55% reduction and annealed for 5 min.

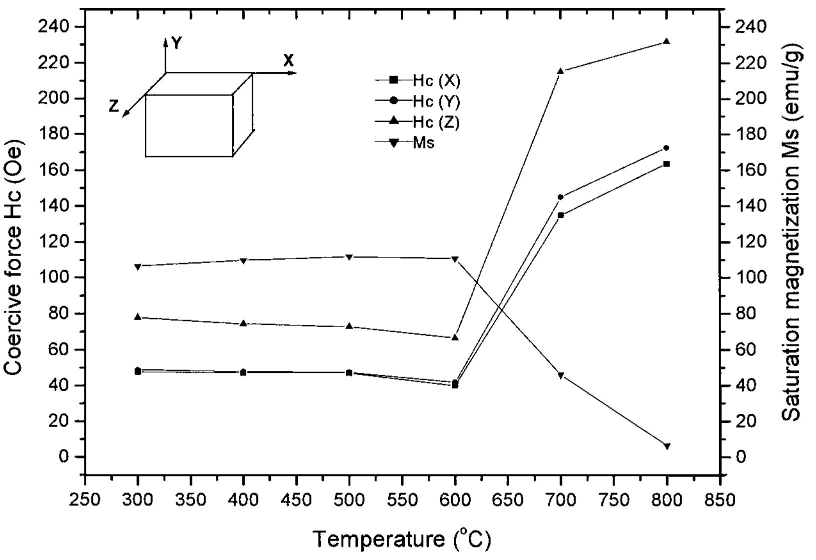


Figure 9 Coercive force and saturation magnetization as a function of temperature for specimens rolled to 55% reduction and annealed for 5 min.

The coercive force measurements are also performed in three directions for each specimen, parallel to the rolling direction (X), perpendicular to the rolling direction (Y) and perpendicular to X and Y direction (Z) as shown in Fig. 9. Fig. 9 shows the coercive force and saturation magnetization as a function of annealing temperature for specimens rolled to 55% reduction in thickness annealed for 5 min. The coercive force depends on the magnetization direction and the results are shown in Table II. Fig. 9 shows that the values of coercive force are higher in Z direction whereas, in X and Y directions of magnetization the values of coercive force are comparable up to 600°C, however, above 600°C coercive force increased in Y direction. The values of coercive force in Z direction are 77.98 and 231.8 Oe at 300 and 800°C, respectively.

The coercive force as a function of annealing time after annealing at temperatures between 600 and 700°C for the specimen rolled to 55% reduction in thickness is shown in Fig. 10. As shown in Fig. 10, coercive force is also affected by the annealing time. For specimens annealed at temperatures between 650 and 700°C the coercive force rises sharply and reaches a maximum value as the annealing time is increased up to 20 min and then decreased with further increase in annealing time. Whereas, annealing at temperatures 600 and 625°C coercive force increases with annealing time reaching maximum up to 80 min at temperature 625°C and 160 min at 600°C and then decreased or remained the same for longer annealing time.

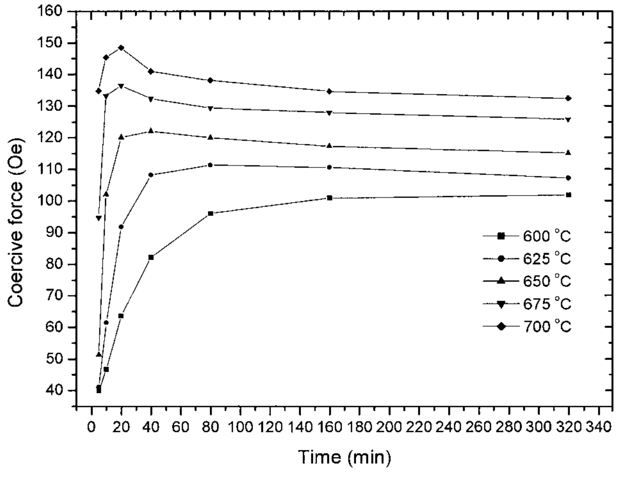


Figure 10 Coercive force as a function of annealing time for specimens rolled to 55% reduction and annealed at 600–700°C.

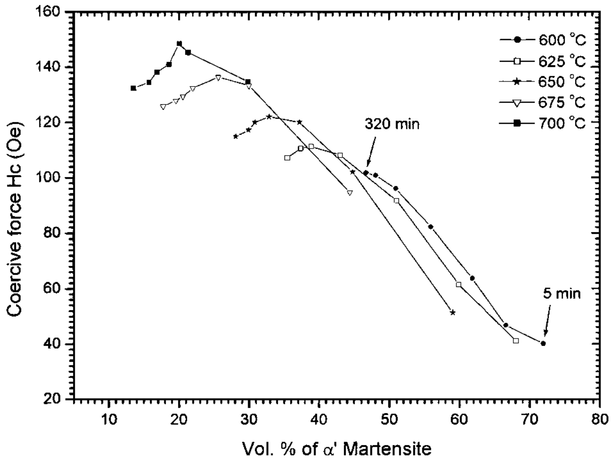


Figure 11 Coercive force as a function of volume percent of α' martensite for specimens rolled to 55% reduction annealed at 600–700°C for time 5–320 min.

Fig. 11 shows coercive force as a function of volume percent of α' martensite for specimens rolled to 55% reduction in thickness after annealing at temperatures between 600 and 700°C for annealing time ranging from 5 to 320 min. As shown in Fig. 11 coercive force depends on annealing temperature, time and volume percent of α' martensite. Annealing at different temperatures for 5 min coercive force shows low values when volume percent of α' martensite are higher (Fig. 11). After annealing at temperatures between 675 and 700°C for 20 min, specimens contain 25.67 and 20.08% of α' martensite respectively, and the values of coercive force are at maximum (Table II). Annealing at 600°C coercive force increased with increased time and decreased volume percent of α' martensite. Whereas, annealing at 625 and 650°C after 80 and 40 min coercive force reached the maximum value with 38.95 and 32.93% α' martensite, respectively. For a long annealing time (above 80 min at 625°C and above 40 min at 650°C), coercive force decreases with the decrease in volume percent of α' martensite (Fig. 11).

3.5. Hardness

Fig. 8b also shows the variations in the hardness as a function of temperature. Hardness curve in Fig. 8b represents the average of several readings on an individual specimen held at a time for the temperature shown. On the section a to b of the hardness curve, where the temperature is below A_s (between 300–600°C) a very slight increase in hardness is observed due to increase in the α' martensite. The drop in the hardness from points b to c is due to development of the reverse α'-γ transformation. The rapid softening at temperature above 700°C is shown by the curve in Fig. 8b is indicative of the recovery and recrystallization process. At temperatures lying between points c and d, the stainless steel is nearly completely non magnetic. The minimum hardness reached corresponds to that of the original austenite.

3.6. Reverse (α'-γ) transformation

The volume percent of α' martensite phase is calculated from the value of saturation magnetization and its reversion to austenite depends on the amount of prior plastic deformation, annealing temperature and time. The absolute amount of reversed γ is estimated by subtracting the volume percent α' martensite measured after rolling reduction to the volume percent of α' martensite obtained after reversion (Table II). Fig. 12 shows volume percent of α' martensite, γ austenite and reversed γ austenite as a function of reduction percent in thickness. The magnetic measurement shows that with the increase in reduction percent in thickness, the volume percentage of α' martensite increases, whereas γ austenite decreases (Fig. 12). Result shows that after 15 and 55% reduction in thickness the induced α' martensitic phase is 5.04 and 67.25%, respectively. Annealing at 700 and 800°C for 5 min resulted in reversion of α' martensite and the transformed reversed γ austenite phase is estimated to be 37.38 and 62.98% respectively, (Table II). Moreover, after annealing at 700 and 800°C the non-reversed volume percent of α' martensite is 29.87 and 4.27%, respectively. Magnetic measurement showed that volume percentage of reversed γ austenite increased with the increase of reduction percent in thickness and annealing temperature, whereas the volume percentage of α' martensite decreased remarably at annealing temperature above 700°C (Fig. 12).

3.7. Scanning electron microscopy

The effects of annealing on microstructures of reverted specimens were also examined. Fig. 13a to f show the scanning electron micrographs of the specimens rolled to 55% reduction in thickness and subsequently annealed at temperatures between 600 to 1100°C for 5 min. Comparing the specimens that are annealed at 600°C to that of the specimens annealed at 700°C, there is a significant difference. The rolling texture is basically not changed during annealing at 600°C (Fig. 13a), however, annealing at 700 and 800°C texture component is reduced (Fig. 13b and c). Unfortunately, it is impossible to obtain the distinct images of the specimens annealed at temperatures between 700 and 800°C and the indications of disappearance of the rolling texture in the reversion of α' martensite to reversed γ austenite is a part of the recovery process. The microstructure of reversed austenite after annealing at temperatures above 800°C, reveals significant changes in structures. The diffuse natures of grains tend to fade out, and recrystallization has started at annealing temperature above 800°C and few small recrystallized grains are distributed in the deformed matrix after annealing at 900°C for only 5 min (Fig. 13d). In addition, after annealing at temperature 1000°C grains coarsening are observed (Fig. 13e). The mean grain size diameter of the specimen after annealing at 1000°C is approximately

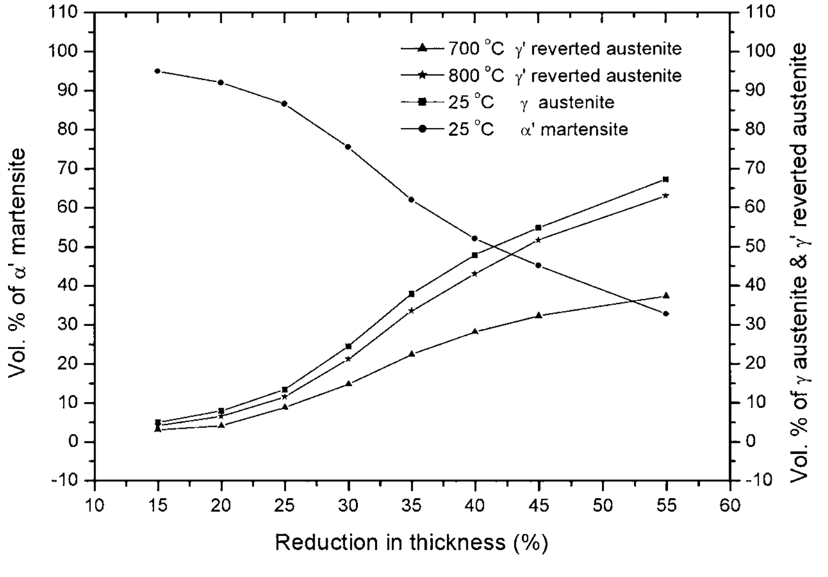
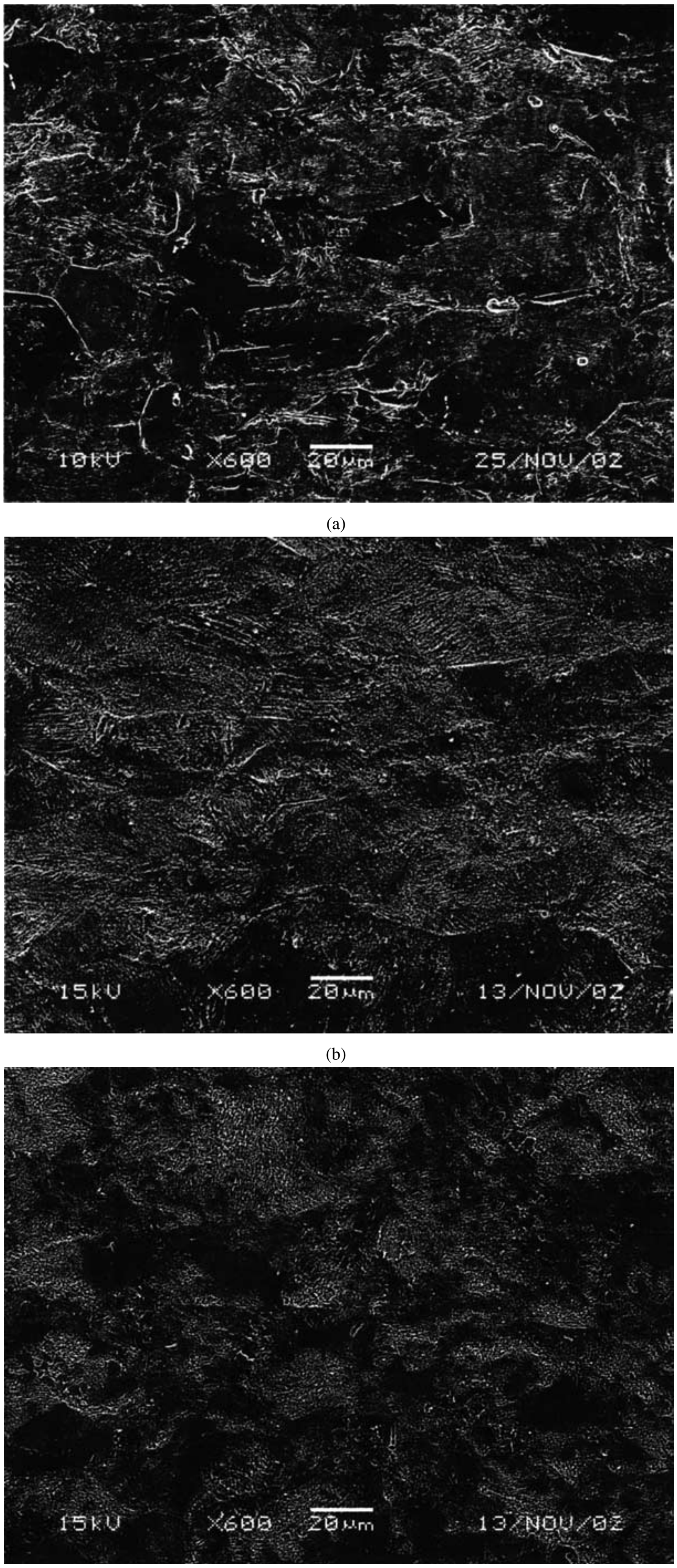


Figure 12 Volume percent of α' martensite, γ austenite and γ' reverted austenite as a function of percent reduction in thickness for specimens annealed for 5 min.

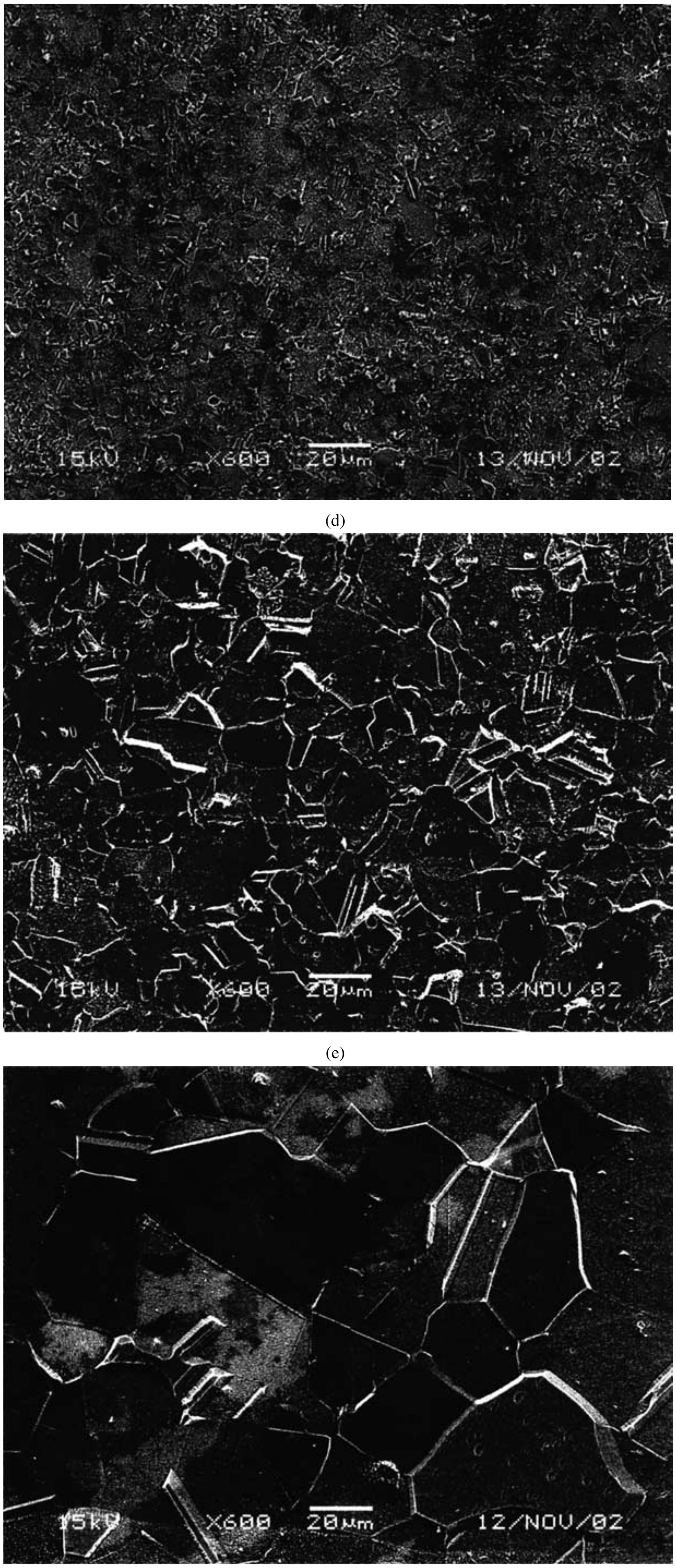


(a)

(b)

(c)

Figure 13 SEM micrographs of specimens rolled to 55% reduction annealed for 5 min. Annealed at temperature: (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C, (e) 1000°C and (f) 1100°C. (*Continued*)



(d)

(e)

(f)

Figure 13 (*Continued*)

15 μm (Fig. 13e). However, when annealed at 1100°C rapid grain growth takes place. Recrystallization may be completed after annealing at 1100°C for 5 min, and the matrix consisted of equiaxed grains with average grain size of about 50 μm (Fig. 13f).

4. Discussion

Magnetic properties are not only dependant on the volume percentage of α' martensitic phase, but also on numerous other parameters which determine the form of α' martensite on micro-scale, such as shape, size, distribution, degree of randomness and coherency in the austenitic matrix. Although the austenitic stainless steel is essentially isotropic, anisotropy may arise due to deformation, martensitic transformation and reversion. The relationship between the saturation magnetization, coercive force, remanence ratio and volume percent of α' martensite with different percent of rolling reductions at room temperature has been previously studied [20]. In this work an analysis has been made relating to reversion of martensite to austenite using magnetic measurements. Austenitic stainless steel cold rolled to 15 to 55% reduction after annealing at various temperatures for times ranging from 5 to 320 min shows considerable changes in magnetic properties. In particular, magnetization, saturation magnetization, coercive force and hardness vary with annealing temperature and time. As a result of rolling reduction there are a large number of deformed grains. These grains may contain high density of dislocations, regions of elastic strain and stored energy. In addition to this, the distribution of grain orientations, or texture is also a parameter of particular significance. The reverse (α'-γ) transformation during annealing of cold rolled stainless steel, and hence its magnetic properties, depends on the above mentioned aspects of the deformed state.

In general, it has been known that intrinsic saturation magnetization is structureinsensitive and depends only on the quantity of ferromagnetic phase in stainless steel. Saturation magnetization is found to be dependent on annealing temperature and time.

Fig. 3a shows the variation in magnetization as a function of magnetic field for the specimens rolled to 55% reduction annealed at various temperatures for 5 min. In the temperatures range 300–600°C the amount of magnetic phase increases on annealing. Maximum increase in the magnetic phase was observed at an annealing temperature of about 500°C.

Annealing at 300–600°C increases the saturation magnetization up to 2–8% in specimens rolled to 45 to 55% reduction (Fig. 4). The saturation magnetization is almost constant at temperatures up to 200°C. Specimen annealed at 500°C shows highest saturation magnetization probably due to the increase in amount of α' martensite phase as has been observed elsewhere [22]. Annealing at temperatures above 600°C causes a reduction in saturation magnetization which is apparently due to transition from the α' martensite phase to a γ austenite as a result of the commencement of reverse (α'-γ) transformation.

The decrease in saturation magnetization in specimens with the largest percent of reduction annealed at 800°C indicates that mechanical deformation has some effect on annealing (Fig. 3b). The greater the deformation causes the less stable martensite structure and the more rapid processes of softening and recrystallization [23]. The specimens rolled to 55% reduction produces an increase in the volume percent of martensite and defect density, and annealing produces an increase in reversed γ austenite and decreases saturation magnetization. Therefore, it might be expected that more highly deformed specimens after reverse (α'-γ) transformation would have a smaller saturation magnetization and decrease in the amount of α' martensite phase.

The relatively small ferromagnetic response detected in the early stages of annealing (300–600°C) is attributable to the following explanations:

1. The increase of α' martensite at 300–600°C is due to nucleation of new particles rather than growth of existing α' martensite particles associated with stress relief [16].
2. Another explanation is that the increase of α' martensite in the range of 300–600°C is due to the precipitation of chromium carbides along the grain boundaries; a zone depleted of Cr and C is formed in the region adjacent to the carbides which reduces the stacking fault energy. The transformation of the α' martensite preferentially occurred in the depleted zone along the grain boundaries which locally increase additional α' martensite formation [24–27] and this explanation is refuted by Guy *et al.* [28].
3. A more likely cause could be the growth of existing α' martensite laths at 300–600°C as the defect structure in the austenite immediately surrounding them recovers, permitting relaxation of the α'/γ interfaces [28].

Specimens with partially α' martensitic structures produced by rolling are annealed for 5 min—a shorter time used to minimize the possibility of chromium carbide precipitation. It seems that with the 5 min annealing time at temperatures between 300–600°C caromium carbide precipitates do no occurr [29]. Moreover, annealing at temperatures between 600–700°C for time ranging from 5 to 320 min also shows decrease in saturation magnetization (Fig. 7). In this study no evidence of such chromium carbide precipitation is obtained by SEM microscopy (Fig. 13a–f). There is no clear explanation for the small increase in α' martensite and hence saturation magnetization at annealing temperatures between 300–600°C. Our results show that the increase in α' martensite at 300–600°C may also depend on following factors:

1. The degree of plastic deformation and hence volume percent of α' martensite present prior to annealing and type of its structure.
2. Stored energy which may be the driving force for recovery and recrystalliaztion.
3. Also may be due to the magnitude of the volume contraction/expansion accompanying the fcc/bcc phase changes.

In analogy with M_s and M_f temperatures for martensitic transformation (where $M_s > M_f$) [30, 31], the reverse transformation is characterized by the A_s and A_f temperatures (where $A_s < A_f$). It is well known that final A_f temperature of the α' martensite to γ austenite reaction on annealing will occur at a temperature where α' martensite is not stable relative to other phases [30]. In this work magnetic technique is presented for the predication of A_s and A_f temperatures. As shown in Fig. 6, in the region II the strong decrease of saturation magnetization is due to the reversion of α' martensite. By using saturation magnetization A_s temperature is found to be between 625–650°C (Fig. 6). And the final A_f temperature is between 900–950°C where saturation magnetization approached to zero for the austenitic stainless steel used in this study.

Annealing below the threshold temperature of the reverse (α'-γ) transformation does not reduce the hardness. The small strengthening effect indicated by the increased hardness on annealing at 300–600°C is attributable to the formation of about 2 to 8% α' martensite (Fig. 8b). And the hardness of the rolled specimens showed an increase of 3–7 HV on annealing in the range of 300 to 600°C. The hardness then began to decrease with increasing temperatures, and above A_f temperature it further decreased towards the hardness of the original austenite or the hardness of as received specimen (Fig. 8b). Hardness results show that the effects of prior transformation appear to be eliminated after annealing at and above 900°C. Removal of ferromagnetic α' martensite phase due to reversion is accompanied by a decrease in saturation magnetization and hardness. Above A_s temperature the hardness dropped substantially as a result of recovery and recrystallization. This is also partly attributable to the fact that the regions of reversed γ austenite have the same crystal structure as the retained γ austenite, and differ only slightly in orientation from one another and from the retained γ, so that less resistance to dislocation movement is offered, as compared with the situation in the α' martensite plus γ austenite structures [32].

In reverse (α'-γ) transformation coercive force is a strong function of annealing temperature and time. The temperature dependence of coercive force is probably due to the easiness of activation of slip systems, rearrangement and movement of dislocations and shape magnetic anisotropy effect. Fig. 8a shows that the coercive force decreases with the amount of prior deformation after annealing at various temperature for 5 min. Specimens rolled to 55% reduction after annealing at various temperatures has the lowest coercive force. It seems that the tendency reported in the work of Ding *et al.* [33] is also observed here: the increase of the amount of martensite, or the increase in saturation magnetization, is accompanied by a decrease of the coercive force. The measurement of coercive force at temperatures between 300–1100°C is shown in Fig. 8b. As shown in Fig. 8b, annealing of the specimen at temperatures between 300–500°C decreased the coercive force as compared to the coercive force of specimen rolled to 55% reduction. This is due to the increase in the amount of α' martensite which may increase resistance to domain wall movement and pinning effect. Fig. 8b also shows that the value of coercive force further decreased at temperatures between 500–625°C and the coercive force reached a minimum value (39.95 Oe) at 600°C. The reasons for this are not yet clear—it seems that when annealed at temperatures between 500–625°C, α' martensite phase remains in the specimens but probably some of the dislocations decrease from the martensite phase, thereby reducing their number density in some volumes of the α' martensite. The net result is that specimen experiences a reduction in coercive force. The measurements also show that there is an increase in coercive force up to 800°C, followed by a sharp decrease in coercive force. There is a large drop in the coercive force at temperature above 800°C. The coercive force shows quite interesting behavior at temperatures between 650–800°C. The manifestation of a significantly enhanced coercive force at annealing temperatures between 650–800°C may be due to shape magnetic anisotropy effect. The reverse (α'-γ) transformation started at 650°C. An interpreation of dislocation mechanisms at temperature between 650–800°C leads one to postulate a recovery proportional to the obstacle density, which seems reasonable. Upon increasing the annealing temperature the effective interaction within the ferromagnetic martensite may decrease and the coercive force stays at its maximum value. Moreover, in the process of recovery high coercive force value may be due to the rearrangement and alignment of domain walls. The microstructures of the specimens annealed at temperatures 700 and 800°C (Fig. 13b and c) also support the recovery process. The disappearance of the elongated grains formed during rolling in the reversion of α' martensite is a part of the recovery process.

Furthermore significant softening occurred on annealing at and above 900°C. Softening of specimens can be induced by recrystallization. It suggests that recrystallization is activated by passage of mobile dislocations and it is possible at high temperature. As the defect density within the grains decreases, the domain wall experiences less pinning forces. Therefore specimen should have lower coercive force. The shape magnetic anisotropy decreases at annealing above 800°C and disappears completely at 1100°C resulting in low coercive force corresponding to softening of specimens.

It seems that when annealed at these temperatures considerable number of dislocations are annihilated. Dislocations are easy to move at higher temperature and also the martensite phase would be difficult to remain at high annealing temperature. The driving force for this is the complete reduction in strain energy stored in the rolled specimens. The influence of rolling direction on coercive force as shown in Fig. 9 has been described elsewhere [20]. The influence of time on the variation of the coercive force was investigated at the temperatures between 600–700°C (Fig. 10). The main variations occur in the initial period of annealing between 5 to 20 min at temperature 675 and 700°C. The increase in coercive force again indicates shape magnetic anisotropy effect.

The above results have shown that magnetic measurements offers the possibility of detecting martensite to austenite reversion in the stainless steel. Detailed studies are currently in progress, which are aimed at establishing a quantitative correlation between dislocations and magnetic properties.

5. Conclusions

Martensite to austenite reversion of austenitic stainless steel with different percent rolling reductions after annealing at various temperatures and times is investigated by magnetic techniques, and the following conclusions can be drawn based on the observations made through this experimental work:

1. Specimens rolled to 40 to 55% reduction after annealing at temperatures between 300 to 625°C for 5 min showed an increase in saturation magnetization in comparison to rolled specimens with same state of reduction.
2. Above 625°C a decrease in saturation magnetization occurs which indicates a reverse (α'-γ) transformation.
3. A_s and A_f temperatures for the reverse (α'-γ) transformation is about 625–650°C and 900–950°C, respectively.
4. Hardness measurements show that softening in the specimen started at temperature above 600°C. The extent of softening for a given temperature is a function of the amount of residual α' martensite.
5. Very low coercive force values are obtained at annealing temperatures between 600–625°C. At temperature above 625°C and up to 800°C coercive force shows highest values. It is attributed to the shape magnetic anisotropy effect. Due to the recovery process internal stresses can be reduced by changing the density and rearrangement of dislocations, and also the effective interaction between the α' martensite phase decreased.

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