Martensitic Transformations of Austenite below 273 K. Dilatometric and Magnetic Studies

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Abstract. The transformation of austenite (Fe-C , Fe-1.5Cr-1C,Fe- N , Fe-Mn-N) to martensite during quenching to the ambient temperature followed by cooling to 77 K was studied with a use of dilatometry and magnetic force measurements. We can see three transformations of austenite. The first during quenching, the second during cooling to 77 K, and the third during an increase of temperature from 77 K to the ambient one. The first 40 minutes of holding at ambient temperature influences most significantly the temperature of the second transformation of austenite. Temperatures of austenite transformation indicated as the increase of magnetic force during the third transformation are lower than that determined by increase of volume (dilatometry). Amounts of austenite transformed during the third transformation determined by magnetic force measurements are somewhat higher than those determined by dilatometry.
The reasons of these differences are discussed on the basis of recent publications.

1. INTRODUCTION

During quenching of Fe-C or Fe-N alloys and steels from austenitizing temperature to a temperature below that , at which the martensitic transformation starts we obtain martensite (M) and a certain amount of retained austenite (RA).The RA can be transformed to the M by subsequent cooling to temperatures below ambient - usually below 273 K. The austenite (A) to M transformation below 273 K has been studied for over last 30 years in numerous publications [1-9]. According to [5-10] during cooling to temperatures about 220 K, M with anomalously low tetragonality is produced. The martensitic transformation at low temperatures produced an additional decrease of the lattice parameter (a) of RA [11] and plastic deformation of the A accompanying the martensitic transformation of high Ni [13]. During heating from temperatures lower than 220 K to the room temperature the tetragonality of „low temperature" M increase to a value close to usual [9].Until now attention has been paid to highly alloyed steels. The aim of this work is to analyse the RA transformations below 273 K in low alloyed steel , alloy Fe- 0.8 wt % N , alloy Fe -1 wt % N - 0.5 wt % C ,and to compare the results with results of earlier works. In certain conditions the RA stabilisation (important for practice of heat treatment) takes place.

2. EXPERIMENTAL

The analysis was performed with a help of an Adamel LK02 quenching dilatometer and a magnetic balance [14]. Tube- like specimens for dilatometric and small rings for magnetic studies were austenitized in preliminary vacuum in the dilatometer, and quenched in the helium gas jet to the ambient temperature. Deep cooling was performed with a help of liquid nitrogen (LN) to temperatures about 77 K. Specimens were prepared from 100Cr 6 steel , alloy Fe - 0.8 wt % N, alloy Fe-1 wt % N - 0.5 wt. % of C . Alloys with N were prepared by gas nitriding, alloys with N+C by gas nitrocarburising [21].
For 100Cr6 steel , four kinds of treatment were applied after austenitizing at 1173 for 10min and quenching: 1. Immediate deep cooling to the LN temperature , and , because of evaporation of nitrogen , heating to the room temperature. 2. Deep cooling to LN , holding at this temperature 10, 25 and 35 min, heating to the room temperature and treatment according to 1. 3. Holding at the room temperature 10, 25, and 35 min and treatment according to 1. 4. Ageing at 323 , 373,

413 and 433 K for 10, 25 and 35 min , cooling to the room temperature and treatment according to 1. The aim of the treatments was to find relation between temperature and time of treatment and Ms temperatures appearing after subsequent cooling below 273 K.

For Fe-N and Fe-N-C alloys after austenitizing at 1043 K (Fe-N) and 1070 K (Fe-N-C) for 5 min and quenching treatment 1 was applied. The stabilisation factor θ , that is difference between Ms_1 and Ms_2 (see Fig.1) was determined for all treatments.

3. RESULTS

A standard dilatometric diagram for majority of deep cooling experiments is presented in Fig. 1 a) and similar magnetic ones in Fig. 2. A dilatometric diagram for specimens of 100Cr6 steel after holding at 77 K is shown in Fig. 1 b)
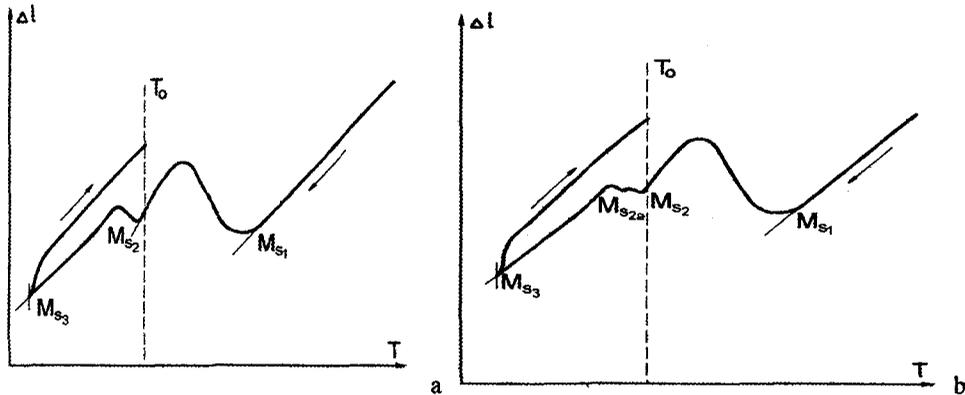
Figure 1. a) Standard dilatometric diagram after quenching and cooling in LN. b) Dilatometric diagram of 100 Cr6 steel after holding at 77 K.

We can see in Fig.1a) - the Ms_1 (increase of volume) temperature obtained during quenching ,the Ms_2 temperature obtained during deep cooling and the Ms_3 temperature obtained during heating from the LN to room temperature. In Fig.1 b) we can see the additional Ms_{2a} temperature appear during deep cooling.

The magnetic diagram (see Fig.2) presents two temperatures for the beginning of the RA transformation to martensite (increase of the force with which the magnet attracts the specimen) - Ms_2 and $Ms_{2'}$. Both appear during deep cooling. The $Ms_{2'}$ transformation starts during cooling and is continued during heating. The change of the Ms_2 temperature, and the factor θ in dependence of holding temperature and time is shown in Fig. 3a and Fig.3b respectively. Changes of the Ms_3 temperature as a function of holding time and temperature is shown in Fig.3 c. The Ms_2 temperature determined with a help of the magnetic method is lower than that determined with a help of dilatometry by about 50 K in the case of 100Cr6 steel and by about 30 K in the case of Fe-0.8 wt% N alloy. The $Ms_{2'}$ temperature appears during magnetic studies just before reaching the L N temperature , at temperature order of 80 K. The total content of the transformed RA determined from dilatometric data (according to the method presented in [14,16]) is lower than that determined form magnetic data (the method presented in [14,15,16]), of the order of 3%.
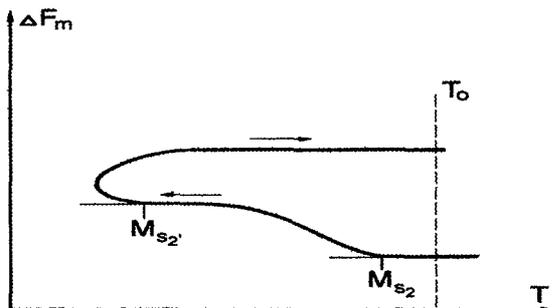
Figure 2. Standard magnetic diagram of specimens after quenching and cooling in LN.
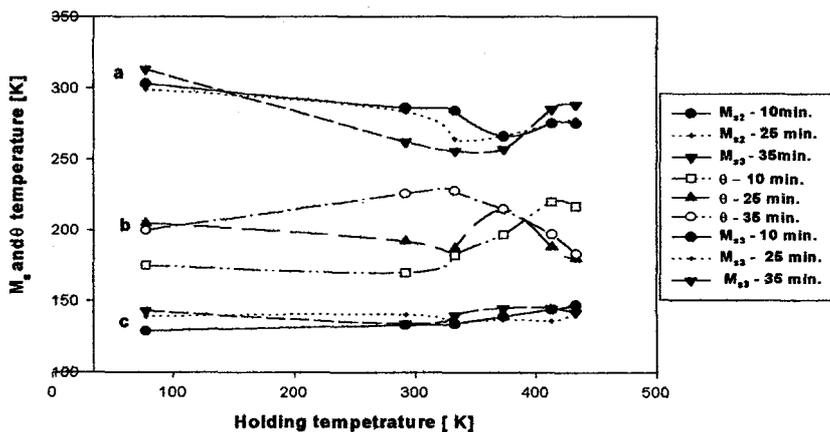
Figure 3. Changes of the Ms_2 temperature (a) , the Ms_3 temperature (c) and the θ factor (b) as a function of holding time and temperature.

4. DISCUSSION

The most surprising result concerns the difference between M_{S2} measured with a help of the magnetic method and the dilatometric one.

The difference appearing in these studies can be caused by the appearance of non (or low) magnetic martensite at the beginning of RA-> martensite transformation , magnetisation will increase with the transformation progress.

Total magnetisation of a ferromagnetic martensite depends on magnetic moment of Fe atoms and on nucleation and ordering of magnetic domains. Paramagnetic properties are identified by magnetometers only if domain ordering appears. Nucleation and domains ordering little depends on the structure of the M [19] but much on the stresses [19,20]. High stresses appear on the ferromagnetic (martensite) /paramagnetic (austenite) grains border [13,11].High stresses should be overcome by magnetic domains passing through the material in order to achieve the ferromagnetic stage. This will only be possible by increase of outside magnetic field, or by higher mobility of atoms. Because of low temperature (below ambient), mobility of atoms is small , higher magnetic field is necessary. This hypothesis was not proved because the increase of the magnetic field was impossible for the instrument applied.

The highest Ms_2 temperature is obtained if holding temperatures are 77 and 433 K by 35 min. (Fig.3). The lowest Ms_2 temperature is obtained for holding temperatures within the range of 291-373 K by 35 min. The stabilisation factor θ is the highest for temperatures order of 291-373 K by 35 min , the smallest for holding time 10 min at 77 and 291 K. The obtained results are in agreement with earlier studies [23,25]. The lowest Ms_2 temperature agrees with the highest θ , the highest Ms_2 temperatures agrees with the lowest θ. A low Ms temperature appears when the RA is resistant to the transformation to martensite , high if the RA is less resistant to the transformation [25-28]. The resistance of the RA to martensite transformation increases if its strength increases [26-28] and austenite strain embryos are not active [21,35-37] .The strength of solid solution increases because of change of composition, inner structure (dislocation density , plastic deformation,) grain refining ,ageing phenomena. The most probable is increase the strength of RA because of increase of interstitials (C, N) content in it [24,26,31,32] , and plastic deformation of the RA regions at the M/RA border [13]. Simultaneously with this the deactivation of the martensite embryo in RA takes place. The deactivation is caused mainly by interstitials segregation to the embryo dislocations [37]. The same influence have the increase of planes number in the thickness of embryo [37] .

On the dilatometric diagram after holding at 433 K by 35 min. we can see a significant contraction [21], that means a significant decrease of specific volume of the specimen. A decrease of specific volume concerns martensite and causes a decrease of compressive stresses in the RA. At the temperature of 433 K carbon can diffuse in the M and the R.A. along dislocations pipes. Carbon could be therefore moved away from M/RA border such that the average content is practically the same , it is proved by one Ms_2 temperature. If certain volumes of the RA on the border of the M/RA are cold deformed at 433 K, recovery of the RA could start and strength of the RA could slightly decrease. There are then, three reasons for high Ms_2 : significant decrease of compressive stresses of the RA , partial recovery of cold deformed the RA , and more homogeneous distribution of C in the RA. Holding specimen at temperature of 77 K gives even a higher increase of Ms_2. We should consider that the dilatometric diagram of the martensitic transformation consist of two parts - one with higher Ms_2 and second with lower Ms_{2a} temperature. According to [10] because of stresses caused by the martensitic transformation the a parameter of the RA is reduced so that the volume of unite cell is smaller of about 1%. The reduction is kept during worming up to the ambient temperature. According to [12] the martensite appearing during cooling to 77 K has a volume smaller than usual , the other studies [29] say that a unit cell volume remains the same. Holding in the LN temperature causes that a part the RA has Ms_2 temperature higher than Ms_{2a} (see Fig.1) of about 20 K. It means that certain processes leading to strength reduction of a part of the RA took place or active austenite strain embryos appeared. The lowest Ms_2 temperature is obtained for holding 35 min. at

temperatures within the range of 291-373 K. The stabilisation factor θ is the highest for this holding conditions. At that temperature range carbon redistribution processes took place in the M [34] and the RA [30]. Carbon redistribution in M in this temperature range may not release compressive stresses within the RA , especially on the M/RA border. These stresses accelerate diffusion of interstitial to dislocations within the RA. That may lead to deactivation of the austenite strain embryo from which martensite transformation starts [30,36,37]. During subsequent cooling much higher undercooling is necessary in order to create austenite strain embryos and start the martensitic transformation.

The lowest Ms_3 temperature was obtained after holding the specimens for 10min in 77 K , the highest after holding at 433 K by 10 min. Because Ms_3 appears during heating, low temperature of transformation means that energy supply necessary to the RA transformation to M is small , high temperature of transformation means that energy supply is big. The RA after holding for 10 min at 77 K is then: compressed less , has the lowest strength , relaxation processes in surrounding the RA the M took place sooner than in other specimens. Holding at 433 K for 10 min stabilise the RA after the second transformation, the RA is then compressed most , it has the highest strength ,the relaxation processes in the surrounding the RA, the M took place later on than in other specimens. Scattering of the other results is so big that it is difficult to find reliable tendency. Results of this studies indicate that in 100 Cr6 steel the RA exists even after holding for 35 min at 77 K , and after second cooling to 77 K.

5. CONCLUSIONS

1. Transformation the RA to the M at temperatures below 273 K proceeds in 100Cr6 steel and in Fe-N and Fe-N-C alloys.
2. The biggest stabilisation of the RA in studied steel was found after holding for 35 min at the temperature range 291-373 K. The results and explanation are in agreement with earlier works.
3. The smallest stabilisation of the RA in studied steel was found after holding for 35 min at 77 and 433 K. Small stabilisation at 433 K was discussed on the basis of earlier works. The most probable explanation is as follows :- the release of compressive stresses of the RA , -beginning of recovery of a cold deformed part of the RA , - and diffusion of carbon leading to a decrease of the carbon gradient in the RA . Small stabilisation at 77 K can be caused by the creation of austenite strain embryos from which the transformation can start.

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