Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 36
ISSUE 1
September
2009

Cold worked high alloy ultra-high strength steels with aged martensite structure

S.J. Pawlak*, H.J. Krztoń
Institute for Ferrous Metallurgy, ul. K. Miarki 12-14, 44-100 Gliwice, Poland
* Corresponding author: E-mail address: spawlak@imz.pl

Received 05.02.2009; published in revised form 01.09.2009

Materials

ABSTRACT

Purpose: The study on structure-property relations of heavily cold worked and aged martensite in two high-alloy structural steels was presented. The aim was to understand properties of the sheet products better and thus extend applications of the newly developed cobalt-free maraging and precipitation hardening stainless steels.
Design/methodology/approach: Mechanical tests were performed on cold rolled and aged specimens. Microstructures were analyzed using TEM and SEM. The crystallographic texture was analyzed by means of X-ray diffraction and ADC method.
Findings: In the process of cold working and ageing both high alloy steels studied could develop yield strength in excess of 1600 MPa. The main strengthening mechanism was precipitation hardening, while work hardening contribution to the strength was very limited. Overaging commences after prolonged treatment above 500ºC, and in both steels could be related to reverted austenite. The texture developed by cold working was the one known as rolling texture type.
Research limitations/implications: In this study the advantage is taken of the high strength that is developed by cold working followed by ageing. Further research is needed for the sheet or strip produced by cold working and annealed before fabrication.
Practical implications: The properties of the high alloy steels studied make them suitable for advanced sheet applications, e.g. as an airborne structural equipment. After welding, strength of the precipitation hardening steels could be largely restored by ageing, because their strength does not rely on strain hardening.
Originality/value: Analysis of the cold worked properties, microstructure and texture, allowed for better understanding of the microstructure-property relationships in the low strain hardening high alloy sheet steels. The results obtained are of practical value for the development, production and manufacture of the ultra-high strength sheet steels.
Keywords: Metallic alloys; High alloy steels; Cold working; Texture and microstructure

Reference to this paper should be given in the following way:
S.J. Pawlak, H.J. Krztoń, Cold worked high alloy ultra-high strength steels with aged martensite structure, Journal of Achievements in Materials and Manufacturing Engineering 36/1 (2009) 18-24.

1. Introduction

Cold working is a common process in the technology of steel production as well as a mean to enhance steel properties or impart a desired shape [1-5]. Particularly often the cold forming operations are used in stainless steel production [6-9]. Very little data exists on cobalt-free maraging steels cold working response [10,11]. The majority of cold rolling operations are carried out to produce sheet or strip with good surface finish and the cold worked product is then softened by an annealing treatment, before fabrication. However, there are applications where advantage is taken of the high strength that is developed by cold working followed by ageing. In the present paper two types of the high alloy martensitic steels precipitation hardened with titanium, based on systems Fe-Ni-Mo-Ti (cobalt-free maraging steel) and Fe-Cr-Ni-Mo-Ti (precipitation hardening stainless steel) were studied. For those steels the combined effects of cold working and precipitation hardening was analysed. These steels have very low work hardening characteristics required for severe cold working processes. The composition of the steels is so balanced that some amount of the residual (retained) austenite may be found on various stages of processing, but the final products should be austenite free. In precipitation hardening stainless steel, apart from austenite, also the delta-ferrite should be avoided, because of its known detrimental effect on the mechanical and corrosion properties. Stainless steels with high work hardening, including metastable steels that undergo rapid transformation from austenite to martensite during working, were described elsewhere [12-15]. While basic properties and microstructures of cobalt-free and other maraging steels in the form of bars were analysed in [16-17].

The crystallographic texture evolution during sequential deformation and heat treatment processes in high strength steels is still not well recognized [10-11, 20], despite its known influence on some mechanical or/and physical properties in many polycrystalline materials [19-20]. In particular, the presence of well defined {111}<uvw> fiber texture (γ-type fibre), is responsible for excellent drawability of an interstitial-free steels. Additionally, the application of orientation distribution function (ODF) analysis enables the detailed study of formation of texture components on every stage of processing, including the dependence on precipitation processes, microstructure, starting texture and the presence of different alloying elements. The properties of the high alloy steels studied make them suitable for advanced applications, e.g. as an airborne structural equipment, made of sheets, particularly for elevated temperatures usage, where lower alloy steels soften rapidly. After welding strength of the precipitation hardening steels can be largely restored by ageing, because their strength rely on ageing rather then strain hardening. This is in contrast to austenitic stainless steels (as e.g. AISI302 18Cr/9Ni grade), which could also develop high strength by cold working, but they have low ductility and irreversibly loose high strength after welding.

2. Material and methodology

2.1. Material

All of the experiments were made with the 78 kg laboratory vacuum melted steels, precipitation hardening stainless (PHSS) and cobalt-free maraging steels, based on the Fe-Cr-Ni and Fe-Ni-Mo matrix, respectively, Table 1.

The steels were first forged to 100 mm square billet, then hot rolled to 40 mm slabs and finally - after annealing and surface cleaning - cold rolled to sheets, without any intermediate anneal. In the form of hot rolled products, as small diameter bars or slabs, the steels studied normally have microstructure of well distinguished prior austenite grain boundaries with packets and laths of martensite, Fig. 1.

Table 1.
Chemical compositions of the high alloy steels studied

Element	PHSS (melt s27)	Co-free maraging steel (melt s26)
C	0.02	0.03
Mn	0.14	0.14
Si	0.06	0.06
P	0.010	0.010
S	0.010	0.010
Cr	10.5	-
Ni	11.7	17.5
Co	-	-
Mo	1.46	4.5
Ti	1.34	1.1
Al	0.05	0.04
N	-	-

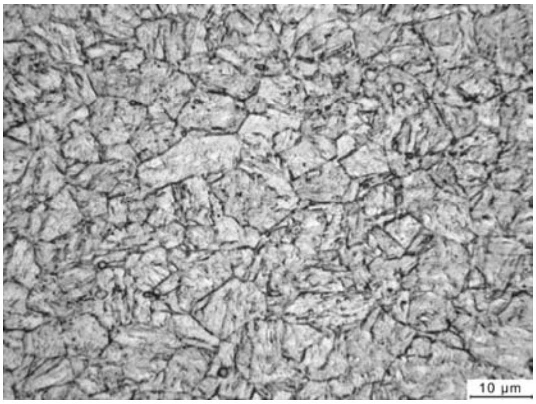


Fig. 1. Microstructure of the cobalt-free maraging steel after hot deformation and heat treatment (annealing and ageing)

2.2. Methodology

The steel microstructure was investigated using routine metallographic procedures of optical, transmission and scanning electron microscopy. Optical microscopy specimens of the cobalt-free steels were prepared by etching in 10% HNO_3, while the precipitation hardening stainless steel specimens were electrolytic etched in 50% HNO_3.

To study the texture, three incomplete X-ray pole figures (110), (200), (211) were collected using Siemens D5005 diffractometer with filtered cobalt radiation and open Eulerian cradle. Schultz reflection technique was used. The measured Chi range was 0º – 70º in steps of 5º and Psi range has been 0º – 355º with 5º increments. The measured pole figures were corrected for defocusation effect and background intensity. ADC method was applied to calculate orientation distribution function (ODF) by means of Labotex software - version 3.0.

Austenite fraction was determined using Averbach-Cohen method. Philips PW 1140 diffractometer with cobalt radiation and graphite monochromator on the diffracted beam was used to measure three pairs of diffraction lines of α and γ phase: $(111)_\gamma$, $(110)_\alpha$, $(200)_\gamma$, $(200)_\alpha$, $(220)_\gamma$, $(211)_\alpha$.

3. Properties and microstructure of cold rolled sheets

Selected cold reductions values during sheet rolling and corresponding values of hardness and austenite content are given in Table 2. Significant amount of austenite was found in the PHSS steel after annealing (~12%). This austenite disappeared in the course of cold deformation. No austenite was observed after annealing in the cobalt-free steel. Only small hardness increase, up to 10%, results from cold rolling of the steels, Table 2. Example of microstructure obtained after cold rolling is shown in Fig. 2, which was very different from that after hot rolling, Fig. 1. Instead of well defined lath martensite structure, the elongated bands are seen.

Table 2.
Cold working data for selected stages of deformation of PHSS steel and cobalt-free steel

Sheet thickness mm	Cold reduction %	Hardness HV	Austenite content %
PHSS steel			
3.6	-	318	12.2
3.3	8	342	<1
1.7	53	357	<1
0.9	74	351	-
Cobalt-free steel			
3.8	-	298	<1
1.8	52	318	<1
2.05	46	331	<1

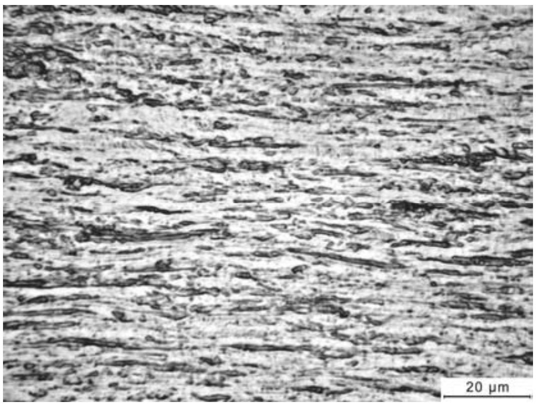


Fig. 2. Microstructure of the PHSS sheet after 74% cold reduction (0.9 mm sheet; polish vertical to sheet surface in the rolling direction)

4. Crystallographic texture of the cold rolled sheets

The texture developed by cold working was the one known as "rolling texture type" found in many metals and alloys with body centered cubic (bcc) crystal structure. The results of texture analysis of both kinds of steels are presented in Figs. 3-4. In Fig. 3, orientation distribution function (ODF) representation of PHSS steel for φ_1 = const, with $\Delta\varphi_1 = 5^{\circ}$ (Fig. 3a) and ODF sections for $\varphi_1 = 0^{\circ}$ (Fig. 3b) and $\varphi_2 = 45^{\circ}$ (Fig. 3c) are presented.

a) b) c)

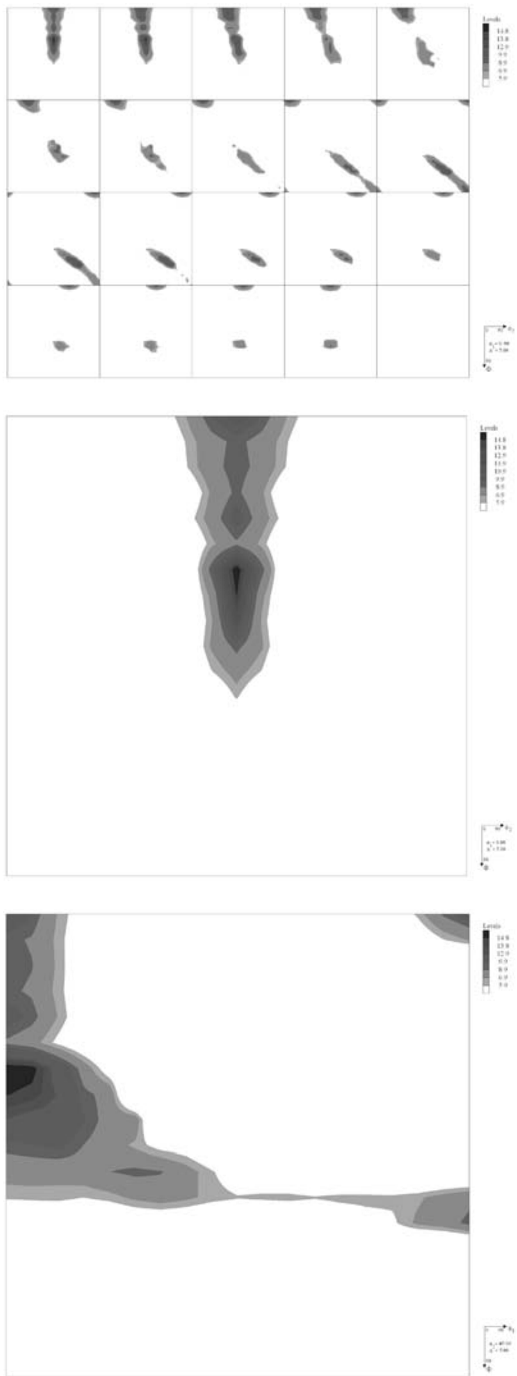


Fig. 3. Orientation distribution function (ODF) representations of the rolling textures of PHSS steel (Fig. 3a – ODF representation for φ_1 = const, with $\Delta\varphi_1 = 5^{\circ}$, Fig. 3b – ODF section $\varphi_1 = 0^{\circ}$, Fig. 3c - ODF section $\varphi_2 = 45^{\circ}$)

a)

b)

c)

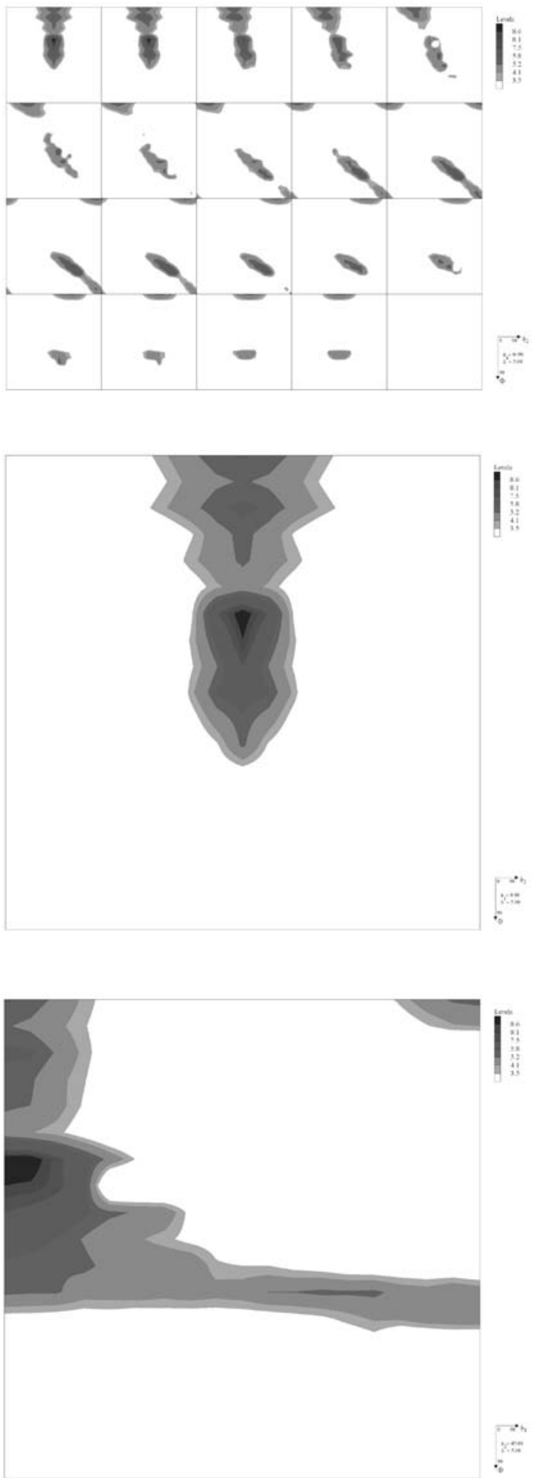


Fig. 4. Orientation distribution function (ODF) representations of the rolling textures of cobalt-free maraging (Fig. 4a – ODF representation for φ_1 = const, with $\Delta\varphi_1$ = 5º, Fig. 4b – ODF section φ_1 = 0º, Fig. 4c - ODF section φ_2 = 45º)

The results of texture analysis of cobalt-free steel are seen in Fig. 4. There are ODF representation of for φ_1 = const, with $\Delta\varphi_1$ = 5º (Fig. 4a) and ODF sections for φ_1 = 0º (Fig. 4b) and φ_2 = 45º (Fig. 4c). In both PHSS steel and cobalt-free steel, the orientations belonging to α fibre, can be identified. The strongest orientation in both kinds of steels is (225)[1 -1 0] and also (337)[1 -1 0] in the vicinity of (225)[1 -1 0]. There is also one common component (001)[1 -1 0]. The weaker additional orientations like (118)[1 -1 0] and (114)[1 -1 0] in PHSS steel and cobalt-free steel are seen, respectively. There are two another weak orientations, not being the components of α fibre, in the sample of PHSS steel, namely (556)[7 -13 5], close to (111)[1 -2 1], and (554)[-2 -2 5]. In the sample of cobalt-free-steel, weak (111)[0 -1 1] component of another typical for bcc metals γ fibre can be identified.

5. Microstructure and properties after rolling and ageing

5.1. Ageing at 480°C and 510°C

To get the highest possible strengths, the cold rolled sheets of both steels were subjected to ageing. Hardness changes (HV30) during ageing at 480°C and 510°C are shown in Figs. 5 and 6.

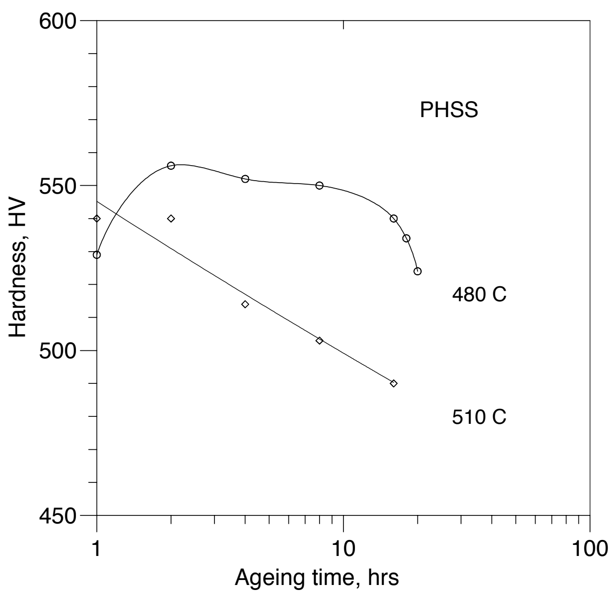


Fig. 5. Hardness (HV30) of the PHSS sheet after cold rolling and ageing at 480°C and 510°C

For ageing temperatures of 480°C and 510°C, most of the hardness increase appeared during first hour of ageing, as is evident comparing hardness values in Table 2 with that in Figures 5 and 6 (180 HV for the PHSS and 120 HV for cobalt-free steel). Maximum hardness in both steel was obtained after ageing at 480°C, while longer ageing at 510°C, e.g. 10 hrs, produced substantial hardness decrease (overaging).

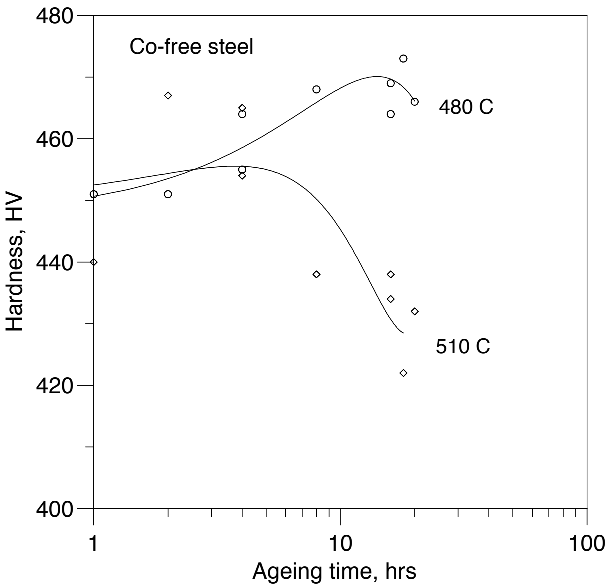
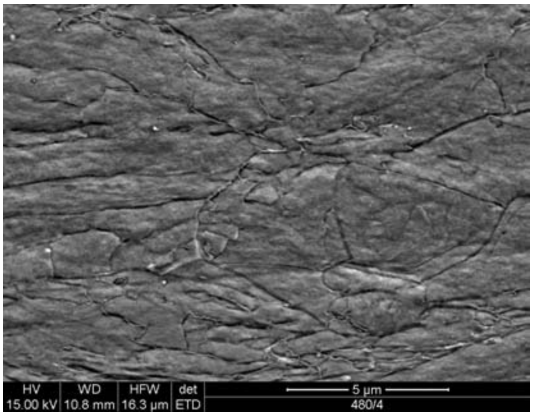


Fig. 6. Hardness (HV30) of the cobalt-free sheet steel after cold rolling and ageing at 480°C and 510°C

a)



b)

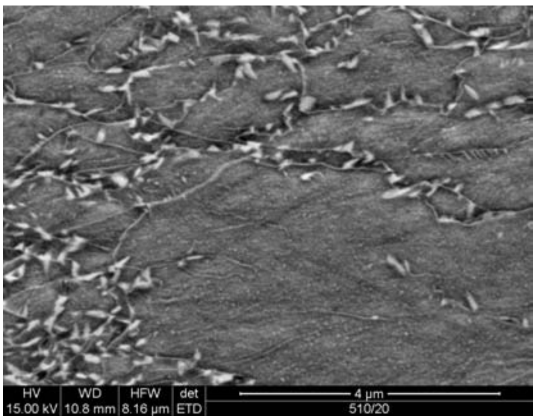


Fig. 7. Scanning electron micrographs of the cobalt-free sheet cold worked 46% and aged at a) 480ºC, 3 hrs,) aged at 510ºC, 20 hrs

X-ray diffraction studies of the overaged steels, 20 hrs at 510°C, revealed presence of the austenite in steel structure (11.7% in PHSS and 7.0% in cobalt-free steel). As the austenite was absent before ageing, Table 2, it may be concluded that it was created as a result of the martensite-austenite (M-A) reaction. The reverted austenite may be the major factor causing gradual strength decrease during prolonged ageing at 510°C in both steels.

Scanning electron microscopy studies of the steel microstructure revealed that after ageing at 480°C no austenite was present, Fig. 7a, while reverted austenite could be clearly observed after long ageing at 510°C, Fig. 7b. The reverted austenite phase, in the form of islands, was predominantly associated with prior austenite grain boundaries, but also nucleated inside the grains.

a) b)

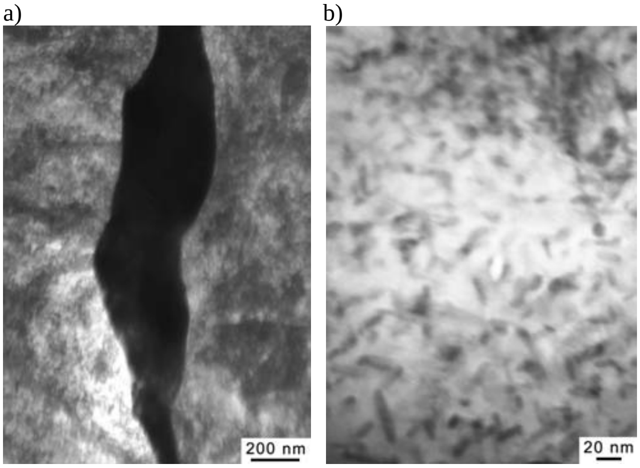


Fig. 8. Transmission electron micrographs of the cobalt-free sheet cold worked 46% and aged at 510ºC, 20 hrs. a) reverted austenite in martensite matrix, b) precipitates in martensite matrix

In the TEM micrographs, Fig. 8 (a), the reverted austenite islands are seen as black elongated grains within matrix of the aged martensite, having high density of tangled dislocations. Despite high thickness of the austenite, resulting from increased resistance to etching, the diffraction patterns revealed reflections form the austenite. When TEM micrographs were taken at very high magnification, the small precipitates in the aged martensite matrix were observed, Fig. 8. The diffraction contrast produced by the precipitates is sometimes called “tweed microstructure”. Such small precipitates with size roughly of 10 x 50 nm, does not seem to be the course of overaging (strength decrease) of the steel, so the argument that reverted austenite is responsible for steel overaging remain valid. On the diffraction patterns, the lattice parameters calculated from the precipitates reflections, were consistent with the intermetallic phase of Ni_3Ti.

5.2. High overageing

In some applications the required tensile elongation is greater than that obtained in this work (below 10%) after heat-treating to the greatest strength. To get substantial increase in tensile elongations, to well over 10%, high overaging was required. For the PHSS, the desired temperature of overaging was about 630ºC, and for the cobalt-free steel 600ºC - at 3 hours of ageing. After that heat treatment the tensile strength of both steels was still high, close to 1200 MPa, Figs. 9-10.

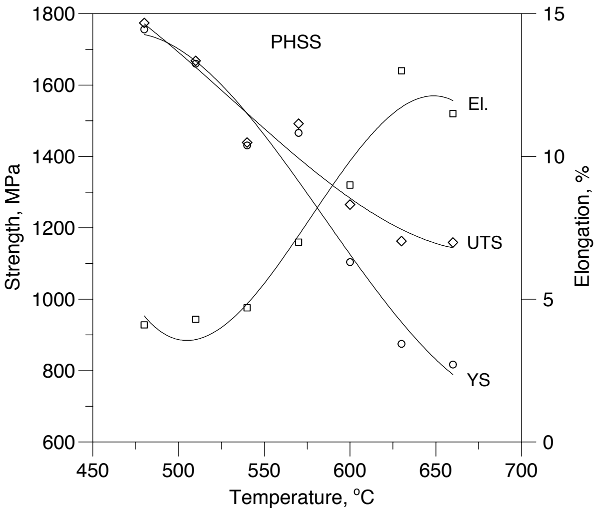


Fig. 9. Tensile properties after cold working and ageing (3 hrs) of the PHSS steel

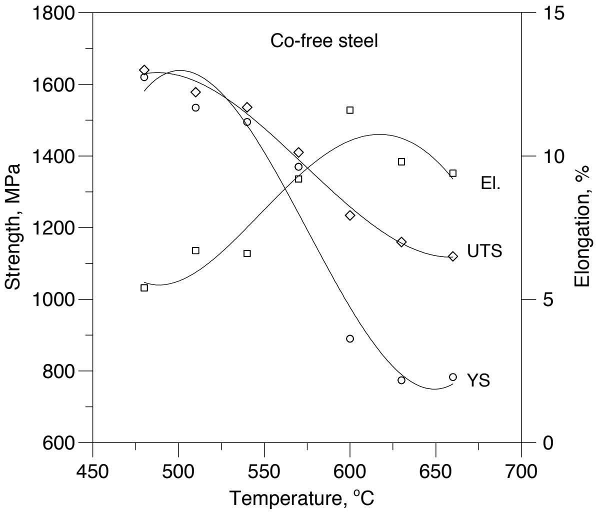


Fig. 10. Tensile properties after cold working and ageing (3 hrs) of the cobalt-free sheet steel

The high strength of the steel may be related to the special microstructure formed at temperatures of high overging. As expected, high amount of austenite was present in the steel microstructure after ageing at 600ºC, Figs. 11 and 12. The austenite phase seen in Fig. 11 has the form of rods or elongated disks, about 1 μm in size, aligned in three directions, two directions lies in the surface and one is perpendicular to the metallographic polish. This metallographic features imply the existence of the crystallographic relation of the austenite phase to former grain, in which it was formed (martensite).

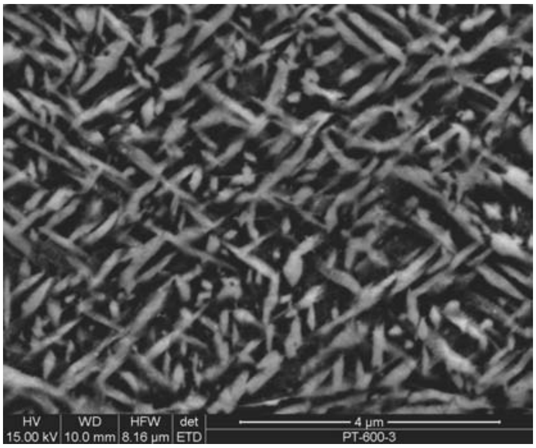


Fig. 11. Scanning electron micrograph of the PHSS sheet aged at 600ºC, 3 hrs

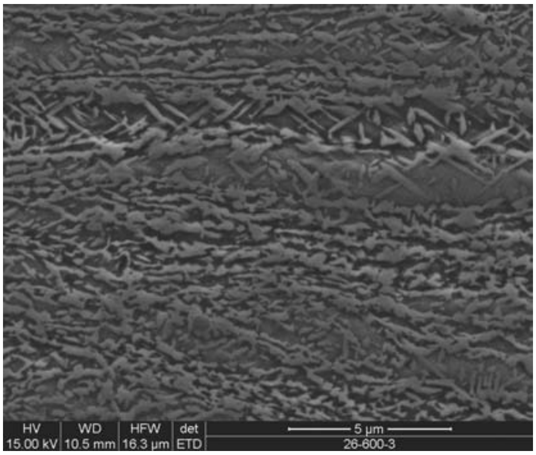


Fig. 12. Scanning electron micrograph of the cobalt-free sheet aged at 600ºC, 3 hrs

What in turn suggests that inverse M-A transformation was diffusionless in nature (shear like transformation). High dispersion of the austenitic phase and nature of the M-A transformation, may serve as a explanation for relatively high strength of the steels after high overaging. Such microstructure as in Fig. 11 occurs only for specially oriented grains. More typical microstructure obtained after high overageing is shown in Fig. 12, where only one narrow band, in the middle of the micrograph, resembles features described above.

6. Conclusions

The study on structure-property relations of heavily cold worked and aged martensite in two high-alloy structural steels Fe-Cr-Ni-Ti and Fe-Ni-Mo-Ti based, was presented, leading to following conclusions:

1. Despite wildly different matrix compositions, Fe-Cr-Ni and Fe-Ni-Mo based, both steels studied showed similar

characteristics in respect of work hardening, response to heat treatment and mechanical properties. In the process of cold working and ageing both high alloy steels studied could develop yield strength in excess of 1600 MPa. The main strengthening mechanism was precipitation hardening, while work hardening contribution to the strength was very limited.
2. The formation of texture components of α fibre after cold rolling was observed in both steels grades. The strongest orientations was the same: (225)[1 -1 0] and also (337)[1 -1 0] in the vicinity of (225)[1 -1 0]. The orientation (337)[1 -1 0] is placed also in the region of (112)[1 -1 0], which was found as one of the main components in cold rolled 18 pct Ni maraging steel by Ahmad et al. [10], and Hosoya et al. [11]. The other components of α fibre are weaker and are different in both steels. The main difference in analyzed textures was the presence in cobalt-free maraging steel, weak (111)[0 -1 1] component of γ fibre.
3. Overaging commences after prolonged treatment above 500ºC, and in both steels could be related to reverted austenite, formed from martensite (M-A transformation). To get tensile elongations over 10% in cold worked steels studied, the high overaging at temperatures of 600-630ºC was required. At these conditions the high tensile strength of about 1200 MPa was still preserved.
4. The work is in progress to study the suitability of the steels with low rates of work hardening for severely forming operations.

Acknowledgements

This work was supported by the Polish Ministry of Science and Higher Education, grant no. R07 034 02.

The authors would like to thank Mr J. Wojtas (M.Sc.) and J. Gazdowicz (Ph.D.) for their help with the electron microscopy.

References

[1] T. Ohashi, H. Chiba, H. Takano, Employment of alumina suspension pad for v-bending of SUS304 strip, Archives of Materials Science and Engineering 30/1 (2008) 57-60.

[2] I. Schindler, M. Janosec, E. Mistecky, M. Ruzicka, L. Cizek, L.A. Dobrzański, S. Rusz, P. Suchanek, Influence of cold rolling and annealing on mechanical properties of steel QStE 420, Journal of Achievements in Materials and Manufacturing Engineering 18 (2006) 231-234.

[3] M. Janosec, J. Schindler, J. Palat, L. Cizek, V. Vodarek, E. Mistecky, M. Ruzicka, L.A. Dobrzanski, S. Rusz, P. Sucharek, Properties of a Nb-V-Ti microalloyed steel influenced by cold rolling and annealing, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 251-254.

[4] L.A. Dobrzański, Metal Engineering Materials, WNT, Warsaw, 2004 (in Polish).

[5] L.A. Dobrzański, Engineering materials and material design. Principles of materials science and physical metallurgy, WNT, Warsaw, 2006 (in Polish).

[6] L.A. Dobrzański, A. Grajcar, W. Borek, Influence of hot-working conditions on a structure of high-manganese austenitic steels, Journal of Achievements in Materials and Manufacturing Engineering 29/2 (2008) 139-142.

[7] S.V. Grachev, L.A. Maltseva, T.V. Maltseva, Effect of high deformations on phase content and hardness of carbon-free stainless steels, Metallovedenie i Termiczeskaja Obrabotka Metalow 1 (2005) 19-23 (in Russian).

[8] M. Milititsky, N. De Wispelaere, R. Petrow, J. E. Ramos, A. Reguly, H. Hanninen, Characterization of the mechanical properties of low-nikel austenitic stainless steels, Materials Science and Engineering A 498 (2008) 289-295.

[9] W. Ozgowicz, E. Kalinowska-Ozgowicz, A. Kurc, Influence of plastic deformation on structure and mechanical properties of stainless steel type X5CrNi18-10, Journal of Achievements in Materials and Manufacturing Engineering 32/1 (2008) 37-40.

[10] Z. Ahmad, M. Farooque, A. Ul Haq, A.Q. Khan, Texture development in dual-phase cold-rolled 18 pct Ni maraging steel, Metallurgical and Materials Transactions A 28/12 (1997) 2459-2465.

[11] Y. Hosoya, Y. Shima, T. Ohkita, A. Nishimoto, Texture formation and aging behaviour in 18% nickel maraging steel cold rolled and austenitized by simulated continuous annealing process, Transactions Iron and Steel Institute of Japan 26 (1986) 798-806.

[12] J. Post, H. Nolles, K. Datta, H.J.M. Geijselaers, Experimental determination of the constitutive behaviour of a metastable austenitic stainless steels, Materials Science and Engineering A 498 (2008) 179-190.

[13] A.K. Raj, K.A. Padmanabhan, Tensile properties and formability of low Ni (1.2 mass%Ni) metastable austenitic stainless steel sheets, Materials Transactions Japan Institute of Metals 39/5 (1998) 613-616.

[14] S.J. Pawlak, The austenite stability in high strength metastable stainless steels, Journal of Achievements in Materials and Manufacturing Engineering 22/2 (2007) 91-94.

[15] M. Ahmed, I. Nasim, S.W.J. Husain, Influence of nickel and molybdenum on the phase stability and mechanical properties of maraging steels, Materials Engineering and Performance 3/2 (1994) 248-254.

[16] S.J. Pawlak, W. Zalecki, Microstructure, properties and hot deformability of the new maraging steels, Journal of Achievements in Materials and Manufacturing Engineering 29/1 (2008) 31-38.

[17] S.J. Pawlak, Microstructure and properties of high-cobalt and cobalt-free maraging steels, Journal of Achievements in Materials and Manufacturing Engineering 27/1 (2008) 31-34.

[18] M. Leonowicz, D. Derewnicka, H. Krztoń, V. Panchanathan, Structural anisotropy in Nd-Fe-B magnets processed by hot working of melt-spun ribbon powder, Proceedings of the Powder Metallurgy World Congress "Powder Metallurgy and Particulate Materials", Orlando, 2002, 14-1-14-10.

[19] D. Derewnicka, H. Krztoń, M. Leonowicz, Texture analysis in die upset forged Nd-Fe-B magnets, Materials Engineering 157-158/3-4 (2007) 247-253.

[20] M.J. Dickinson, S.D. Gray, Influence of precipitation hardening and reversible martensite reactions on recrystallization textures of 17%Ni-8%Co-4%Mo steel, Journal of Applied Crystallography 4 (1971) 452-461.