

STEEL ARTICLE

TECHNICAL FIELD

5 The invention concerns an article made of steel having features which are desirable for plastic mould steels intended to be used for any of the following fields of application:

- elements, e.g. screws and barrels for feeding and conducting plastic masses in machines for the manufacturing of plastic components, e.g. elements in injection
10 moulding and extrusion assemblies, and
- mould tools and tool parts for injection moulding of plastic materials.

Particularly the invention concerns objects of steel having excellent wear resistance, good corrosion resistance, hardenability, and tempering resistance as well as adequate
15 toughness; features which make the steel suitable to be employed within said fields of application. The use of steel articles according to the invention, however, is not limited to said fields of application but can be employed also for a variety of other applications, where said features are necessary or desirable, e.g. details in pumps for feeding wearing media and for wear parts in machines and other equipments, just to mention some.

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BACKGROUND OF THE INVENTION

For parts of the above mentioned fields of application there is today used a steel which is known under the trade name ELMAX™, which is a high alloyed, powder metallurgy manufactured chromium-vanadium-molybdenum steel having good wear resistance and
25 corrosion resistance. The steel has the following nominal chemical composition in weight-%: 1.7 C, 0.8 Si, 0.3 Mn, 18.0 Cr, 1.0 Mo, 3.0 V, balance iron and impurities. The steel has a high wear resistance and corrosion resistance, which makes a manufacturing of moulds for plastic moulding having a long working life possible. The steel is used e.g. in the electronic industry for the manufacturing of couplings, contacts,
30 resistances, and integrated circuits, but can also be used in the food industry, where corrosion resistance is required from sanitary reasons, at the same time as the wear resistance is an essential factor.

However, there is a demand for a steel having a still better combination of excellent
35 wear resistance, hardenability, tempering resistance, and corrosion resistance, particularly for elements such as screws and barrels for feeding and conducting plastic masses in equipments for injection moulding of plastic materials.

DISCLOSURE OF THE INVENTION

It is the purpose of the invention to provide steel articles which satisfy the above mentioned demands. This can be achieved therein that the article is manufactured of a spray formed steel material having a chemical composition in weight-% and with a micro-structure which are stated in the appending patent claims.

Further, as far as the alloy elements which are included in the steel are concerned, the following applies.

- Carbon shall exist in a sufficient amount in the steel in order, in the hardened and tempered condition of the steel, to form, in combination with vanadium, 3-8 vol-% MC-carbides, in which M substantially is vanadium and, in combination with chromium, 10-20 vol-% M_7C_3 -carbides, in which M substantially is chromium, the total amount of MC-carbides and M_7C_3 -carbides amounting to 14-25 vol-%, and also exist in solid solution in the martensitic matrix of the steel in the hardened condition in an amount of 0.2-0.7 weight-%, preferably 0.3-0.6 weight-%. Suitably the amount of dissolved carbon in the matrix of the steel is about 0.5%. The total amount of carbon in the steel, i.e. carbon which is dissolved in the matrix of the steel plus the carbon that is bound in carbides shall be at least 1.7%, preferably at least 1.8%, while the maximum content of carbon may amount to 2.5%, preferably not more than 2.3%.

- The article of the invention is manufactured by a technique which includes spray forming, in which drops of molten metal are sprayed against a rotating substrate on which the drops rapidly solidify to form a successively growing ingot. The ingot then can be hot worked by forging and/or rolling to desired shape. At the solidification of the drops said carbides are formed, which are evenly distributed in the ingot and thence in the final product. Due to the controlled rate of solidification of the drops, which is slower than during manufacturing of metal powder by atomising a stream of molten metal and rapid cooling of the formed droplets, but essentially more rapid than during conventional ingot manufacturing, continuous casting and/or ESR-remelting, the carbides have sufficient time to grow to a size which has turned out to be very favourable in the article according to the invention. Thus the MC-carbides can be caused to achieve an essentially rounded shape, such that at least 80 vol-% of the MC-carbides obtain a size in the longest extension of the carbides amounting to 1-10 μm , preferably at least 5 μm , while the M_7C_3 -carbides typically achieve a more elongated shape than the MC-carbides, such that at least 80 vol-% of the MC-carbides get a maximum extension which amounts to 3-50 μm , preferably at least 10 μm .

Nitrogen optionally may be added to the steel in connection with the spray forming to a maximal amount of 0.20%. According to the preferred embodiment of the invention, however, nitrogen is not intentionally added to the steel but will nevertheless exist as an unavoidable element in an amount of max 0.15%, normally max 0.12%, and is then not a harmful ingredient. To the contrary, the nitrogen may have a favourable effect by forming vanadium and chromium carbonitrides in combination with carbon. Thus a minor fraction of carbonitrides may be included in the above mentioned volume contents of MC- and M_7C_3 -carbides.

10 Silicon is present as a residue from the manufacturing of the steel and exists normally in an amount of at least 0.1%, preferably at least 0.2%. The silicon increases the carbon activity in the steel and therefore contributes to affording the steel an adequate hardness without causing embrittlement problems. Silicon, however, is a strong ferrite former and must therefore not exist in amounts above 2.0%. Preferably, the steel does not contain more than max 1.0% silicon.

Manganese also exists as a residue from the manufacturing of the steel and binds the low amounts of sulphur which may exist in the steel by forming manganese sulphide. Manganese therefore should exist in an amount of at least 0.1%, preferably in an amount of at least 0.2%. Manganese also promotes the hardenability, which is favourable, but must not exist in amounts above 2.0% in order to avoid embrittlement problems. Preferably, the steel does not contain more than max 1.0% Mn. A nominal content of manganese is 0.5%.

25 Chromium shall exist in an amount of at least 12%, preferably in an amount of at least 13% in order to afford the steel a desirable corrosion resistance. Further chromium is an important carbide former and forms M_7C_3 -carbides together with carbon, which carbides in combination with the MC-carbides contribute to a desired wear resistance. Chromium also strongly promotes the hardenability. The term hardenability means the capacity of achieving a high hardness more or less deep in the article that shall be hardened. The hardenability shall be sufficient for the article to be through hardened even if the article has comparatively large dimensions, without employing very rapid cooling in oil or water at the hardening operation, which might cause dimension changes. The hardness in the steel shall be at least 55 HRC, suitably 58-64 HRC, after tempering. Chromium, however, is a strong ferrite former. In order to avoid ferrite after hardening from 1020-1150°C, the chromium content must not exceed 16%, preferably max 15.5%. A suitable chromium content is 13.2-14.5%, nominally 14.0%.

Vanadium shall exist in the steel in an amount of 5.0-8.0% in order, together with carbon and possibly nitrogen, to form said MC-carbides or carbonitrides in the martensitic matrix of the steel in the hardened and tempered condition. Preferably, the steel contains at least 6.1% and max 7.5% V. A suitable vanadium content is 6.3-7.3%,
5 nominally 6.8% V.

In principle, vanadium may be replaced by niobium for the formation of MC-carbides, but for this twice as much niobium is required as compared with vanadium, which is a drawback. Further, niobium has the effect that the carbides will get a more edgy shape
10 and be larger than pure vanadium carbides, which may initiate ruptures or chippings and therefore reduce the toughness of the material. This may be particularly serious in the steel of the invention, the composition of which has been optimised for the purpose of achieving an excellent wear resistance in combination with a high hardness and tempering resistance, as far as the mechanical features of the material are concerned.
15 The steel therefore must not contain more than max 0.1% niobium, preferably max 0.04% niobium. According to the most preferred embodiment, niobium is tolerated only as an unavoidable impurity in the form of a residual element from the raw materials which are used in connection with the manufacturing of the steel.

20 Molybdenum shall exist in an amount of at least 2.1%, preferably at least 2.3%, in order to afford the steel a desired hardenability in combination with chromium and the limited amount of manganese. Molybdenum also contributes to the corrosion resistance of the steel but is a strong ferrite former. The steel therefore must not contain more than 3.5% Mo, preferably max 3.0, suitably max 2.5%.

25 In principle, molybdenum may completely or partly be replaced by tungsten, but for this twice as much tungsten is required as compared with molybdenum, which is a drawback. Also the use of any scrap will become more difficult. Therefore tungsten should not exist in an amount of more than max 1.0%, preferably max 0.5%. Most
30 conveniently, the steel should not contain any intentionally added tungsten, which according to the most preferred embodiment of the invention is tolerated only as an unavoidable impurity in the form of a residual element from the raw materials which are used in connection with the manufacturing of the steel.

35 Besides the mentioned alloy elements the steel does not need, and should not, contain any more alloy elements in significant amounts. Some elements are definitely undesired, because they may have an undesired influence on the features of the steel.

This is true, e.g. as far as phosphorus is concerned, which should be kept at as low level as possible, preferably at max 0.03%, in order not to have an unfavourable effect on the toughness the steel. Also sulphur in most respects is an undesired element, but its negative effect on, in the first place, the toughness, essentially can be neutralised by means of manganese, which forms essentially harmless manganese sulphides, wherefore sulphur may be tolerated in a maximal amount of 0.2% in order to improve the machineability of the steel. Preferably, the steel, however, normally does not contain more than max 0.1%, preferably max 0.05% sulphur.

Further features and aspects of the invention will be apparent from the following description of performed experiments and from the appending patent claims.

BRIEF DESCRIPTION OF DRAWINGS

In the following description of performed experiments, reference will be made to the accompanying drawings, in which

- Fig. 1 is a photography which shows the micro-structure of a portion of an article according to the invention,
- Fig. 2 shows tempering curves for a number of examined steel alloys,
- Fig. 3 shows a section of the curves of Fig. 2 at a larger scale,
- Fig. 4 in the form of a chart illustrates the hardenability of a steel according to the invention and of two reference materials with data from CCT- diagrams,
- Fig. 5 shows the abrasive wear resistance of a steel according to the invention and of two reference materials, and
- Fig. 6 illustrates the corrosion resistance of the examined materials in the form of the corrosion current, I_{cr} , from the polarisation curves of the materials.

DESCRIPTION OF PERFORMED TESTS

Materials

The chemical compositions of the materials which are included in the test series are stated in Table 1. Steels No. 1 and 2 are reference materials. Both are powder metallurgy manufactured. Steel No. 1 is a commercial steel of type ELMAX™, which has been mentioned in the description of the background of the invention, and steel No. 2 is another commercially available steel. Steels No. 3A and No. 4A refer to aimed compositions, while steel No. 3 and No. 4 are analysed compositions of two steels, the contents of vanadium of which lie in the lower and the upper section, respectively, of the widest aspects of the chemical composition of the steel of which the article

according to the invention is made. The steels 3 and 4 have been manufactured by the so called spray forming technique, which also is referred to as the OSPRAY-method, according to which an ingot, which rotates about its longitudinal axis, successively is established from a molten material which in the form of drops which are sprayed
 5 against the growing end of the ingot that is produced continuously, the drops being caused to solidify comparatively rapidly once they have hit the substrate, however not as fast as when powder is produced and not as slow as in connection with conventional manufacturing of ingots or in connection with continuous casting. More specifically, the drops are caused to solidify so rapidly that formed MC- and M₇C₃-carbides will grow
 10 to the desired size according to the invention. The spray-formed ingots of steel No. 3 and of steel No. 4 had a mass of about 2.9 and about 2.2 tons, respectively. The diameter of the ingots was about 500 mm.

The spray-formed ingots of steel No. 3 and steel No. 4 were heated to a forging
 15 temperature of 1100°C and were forged to the shape of blanks for further examinations.

Table 1 Chemical composition, weight-%

Steel, No.	C	Si	Mn	S	Cr	Mo	V	Nb	N	Balance
1	1.71	0.84	0.30	0.019	17.9	1.08	3.01	0.015	0.104	Fe and unavoidable impurities
2	2.41	0.29	0.43	0.019	13.1	1.12	7.91	0.003	0.083	-"-
3A*	1.85	0.50	0.40	≤ 0.020	14.0	2.30	6.00	-	≤ 0.10	-"-
3	1.93	0.61	0.39	0.019	13.7	2.32	5.64	0.02	0.10	-"-
4A*	2.35	0.50	0.40	≤ 0.020	14.4	2.30	8.20	-	≤ 0.10	-"-
4										-"-

20 * Aimed compositions

In the studies which shall be explained in the following, steels No. 1, 2 and 3 were tested with reference to

- micro-structure
- 25 • hardness versus austenitising and tempering temperature
- hardenability
- ductility

- abrasive wear resistance
- corrosion resistance

Micro-structure

- 5 The micro-structure of steels No. 1 and 2 is typical for powder metallurgy manufactured steels, which implies that all carbides are very small, max about 3 μm , and evenly distributed in the matrix of the steel independent of its heat treatment. The micro-structure in the hardened, $T_A = 1120^\circ\text{C}/30 \text{ min.}$ and tempered, $525^\circ\text{C}/2 \times 2 \text{ h.}$ condition, of steel No. 3 is apparent from Fig. 1, which shows a portion in the centre of an
- 10 examined bar having the cross section $350 \times 63.5 \text{ mm}$. In the matrix of the steel, which consists of tempered martensite, there are primary carbides of MC-type having a typically rounded shape and a size of from about 1 μm up to max about 10 μm , and chromium carbides, M_7C_3 , having a substantially more extended shape. The size of the chromium carbides was max about $15 \times 50 \mu\text{m}$ in the centre of the bar. In the surface of
- 15 the bar, which also was examined but which is not shown in any picture, the MC-carbides as well as the chromium carbides were somewhat smaller; up to about 6 μm and up to about $8 \times 30 \mu\text{m}$, respectively. A macro-etched cross section of the rod also evidenced that the structure is very even over the whole cross section.
- 20 The carbide content was examined by the point calculation method in a scanning electron microscope. The measured total content of carbides in steel No. 3 was 20.4%, of which 15.4% were rich in chromium (M_7C_3) and 5% were rich in vanadium (MC). As far as steel No. 2 is concerned, the measured total content of carbides was 23.9 vol-%, of which 13.1% were rich in chromium (M_7C_3) and 10.8% were rich in vanadium
- 25 (MC). The measured total content of carbides in steel No. 1 was 14%, of which 13% were rich in chromium (M_7C_3) and 1% was rich in vanadium (MC). All carbide contents refer to vol-%. The heat treatment condition was $T_A = 1120^\circ\text{C}/30 \text{ min.} + 250^\circ\text{C}/2 \times 2 \text{ h}$ for steel No. 2 and steel No. 3 and $T_A = 105^\circ\text{C}/30 \text{ min.} + 250^\circ\text{C}/2 \times 2 \text{ h}$ for steel No. 1.

30 Hardness after heat treatment

- In the soft annealed condition, the steel according to the invention has a hardness (Brinell-hardness) of 200-300 HB, typically about 250 HB. The influence of the tempering temperature on the hardness after austenitising between 1080 and 1150°C is shown in Fig. 2. Steel No. 3 exhibits a stronger secondary hardening than the two
- 35 reference steels 1 and 2 after austenitising at 1120 and 1150°C and reaches a hardness of 63 HRC after tempering at $525^\circ\text{C}/2 \times 2 \text{ h.}$ A section of the region which comprises the hump on the tempering curves is shown at a larger scale in Fig. 3. Steel No. 2 had the

same hardness as steel No. 1 after austenitising at 1120°C, but a substantially lower tempering resistance than both steel No. 1 and No. 3.

Hardenability

- 5 The hardness versus the required time for cooling from 800 to 500°C is shown graphically in Fig. 4. It is apparent from this chart that the hardenability of steel No. 3 is significantly better than that of steel No. 1 and much better than that of steel No. 2.

Toughness

- 10 The impact energy was examined, un-notched test specimens being used after hardening from $T_A = 1120^\circ\text{C}/30$ min for steels Nos. 2 and 3, and from $T_A = 1100^\circ\text{C}/30$ min, respectively, for steel No. 1 after varying tempering temperatures between 200 and 550°C. The dimension of the bar of the examined steel, however, varied, wherefore the results are not fully comparable. However, it could be settled that the impact energy of
15 all examined steels exceeded 10 J for all longitudinal samples, which satisfies the criteria as far as approvable impact toughness is concerned for the intended field of application of the article according to the invention.

Abrasive wear

- 20 The wear resistance was examined in the form of a pin-to-pin test using SiO_2 as an abrasive agent. As far as the dimensions and hardening temperatures of the examined samples are concerned the following applies. Steel No. 1: $\varnothing 38$ mm/ $T_A = 1100^\circ/30$ min; steel No. 2: $\varnothing 37$ mm/ $T_A = 1120^\circ\text{C}/30$ min; steel No. 3: 350×63.5 mm/ $T_A = 1120^\circ\text{C}/30$ min. The results are apparent from the bar chart in Fig. 5. This chart:
25 illustrates that steel No. 3 for all tempering temperatures exhibited the by far best wear resistance.

Corrosion resistance

- The corrosion resistance was measured via potential curves in 0.05 M H_2SO_4 , pH = 1.2.
30 I_{cr} at the active peak defines the relative corrosion resistance, which means that the corrosion current should be as low as possible. In the bar chart in Fig. 6, the different materials are compared as a function of the heat treatment condition. Steel No. 3 had the best corrosion resistance after tempering up to at least 400°C. After tempering at 525°C, the corrosion resistance was reduced for all examined materials; steel No. 3 slightly
35 more than steel No. 2 and considerably more than steel No. 1. It should, however, be observed, as far as this comparison is concerned, that steel No. 3 after tempering had an essentially higher hardness than the comparative materials.

DISCUSSION

The described tests show that of steels according to the invention there can be manufactured articles having a very high wear resistance, which can be attributed to a combination of the hardness of the steel and its content of carbides in a sufficient amount and of sufficient size. Another important factor is the hardenability of the steel, which is very good and better than comparable steels. Hardnesses of between 59 to 62 HRC in combination with an excellent corrosion resistance were measured after tempering at 200 and 400°C and hardness of between 61 to 63 HRC after tempering at 500°C. By tempering at about 525°C there can be achieved a hardness peak of between 61 to 64 HRC. In the latter case some corrosion resistance is lost, but the high hardness can be utilised for certain applications where high requirements on the corrosion resistance do not exist. The invention thus provides a pronounced flexibility with reference to the adaptability of the usefulness of the steel for various applications by choice of a suitable heat treatment. Another important factor for the usability of the steel is its manufacturing, which is based on the spray forming technique, which is essentially more economical than powder metallurgy manufacturing.

It should also be realised that the article according to the invention may have any conceivable shape, including spray formed ingots, blanks in the form of, e.g., plates, bars, blocks, or the like, which normally are delivered by the steel manufacturer in the soft annealed condition with a hardness of 200-300 HB, typically about 250 HB to the customers for machining to final product shape, as well as the final product which has been hardened and tempered to intended hardness for the application in question.

CLAIMS

1. Steel article, characterised in that it consists of an alloy which contains in weight-%
1.7-2.5 C
5 0.1-2.0 Si
0.1-2.0 Mn
max 0.2 N
max 0.2 S
12-16 Cr
10 2.1-3.5 (Mo + W/2)
5-8 V
max 0.1 Nb
balance essentially only iron and unavoidable impurities, and that the steel has a micro-structure obtainable by a manufacturing of the steel which comprises spray forming of
15 an ingot, the micro-structure of which contains 14-25 vol-% carbides of mainly MC-type, where M substantially consists of vanadium, of which carbides at least 80 vol-% have a substantially rounded shape and a size in the longest extension of the carbides amounting to 1-10 μm , and M_7C_3 -carbides, where M substantially consists of chromium, which carbides typically have a more elongated shape than the MC-carbides,
20 of which MC-carbides at least 80 vol-% have a maximal extension amounting to 3-50 μm .
2. Article according to claim 1, characterised in that the micro-structure contains 3-8 vol-% MC-carbides and 10-20 vol-% M_7C_3 -carbides.
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3. Article according to claim 2, characterised in that it after hardening and tempering has a hardness of 55 to 64 HRC.
4. Article according to claim 3, characterised in that the martensitic matrix of
30 the steel after hardening and tempering contains 0.2-0.7 weight-% C in solid solution.
5. Article according to any of claims 1-4, characterised in that the total content of C in the steel is at least 1.8%.
- 35 6. Article according to any of claims 1-4, characterised in that the total content of C in the steel is max 2.3%.

7. Article according to any of claims 1-6, characterised in that the steel contains 0.2-1.0% Si.
8. Article according to any of claims 1-7, characterised in that the steel contains 0.2-1.0% Mn.
9. Article according to any of claims 1-8, characterised in that the steel contains at least 13% Cr.
10. Article according to any of claims 1-9, characterised in that the steel contains max 15.5% Cr.
11. Article according to claim 10, characterised in that the steel contains 13.2-14.5% Cr.
12. Article according to any of claims 1-10, characterised in that the steel contains at least 6.1% V.
13. Article according to any of claims 1-11, characterised in that the steel contains max 7.5% V.
14. Article according to claims 12 and 14, characterised in that the steel contains 6.3-7.3% V.
15. Article according to any of claims 12-14, characterised in that the steel does not contain more than max 0.04 Nb.
16. Article according to any of claims 1-15, characterised in that the steel contains at least 2.3% Mo.
17. Article according to any of claims 1-15, characterised in that the steel contains max 3.0% Mo.
18. Article according to any of claims 1-17, characterised in that the steel does not contain more than max 1.0% W, preferably max 0.5% W.

19. Article according to any of claims 1-18, characterised in that the steel does not contain more than max 0.1% S, preferably max 0.05% S.
20. Article according to any of claims 3-19, characterised in that it after
5 hardening and tempering at a temperature between 180-220°C has a hardness of 55-62 HRC, preferably at least 59 HRC.
21. Article according to any of claims 3-19, characterised in that it after
hardening and tempering at a temperature between 380 and 450°C has a hardness of 55-
10 62 HRC, preferably at least 59 HRC.
22. Article according to any of claims 3-19, characterised in that it after hardening from a temperature between 480 and 520°C has a hardness of 60-63 HRC.
- 15 23. Article according to any of claims 3-19, characterised in that it after hardening from a temperature between 510 and 530°C has a hardness between 61 and 64 HRC.