МАТЕРИАЛОВЕДЕНИЕ И ТЕРМИЧЕСКАЯ ОБРАБОТКА МЕТАЛЛОВ

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EFFECT OF INTERCRITICAL QUENCH HARDENING ON MECHANICAL PROPERTIES OF 11% CR STEEL

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Abstract

The paper is devoted to the study of the possible use of corrosion- and heat-resistant steel grade 13Kh12N2W2MF (0.14% C; 10.8% Cr; 1.5% Ni; 1.9%W; 0.4% Mo; 0.3% V) for production of locking devices and parts of oil pumps. Technical specifications for the steels of this class require corrosion resistance, V-notch impact toughness at –60°C (KCV^{-60}) to be 24.6 J/cm^2 or higher, and yield and ultimate tensile strength greater than 650 and 800 MPa, respectively. The difficulty is that the parts have different weight and, consequently, different cooling rates after high-temperature tempering. Slow cooling of massive parts made of high-chromium steels may produce temper brittleness intensified by carbide precipitation, which dramatically decreases impact toughness. The first part of the study is about the effect of tempering temperature on room-temperature mechanical properties of the steel grade. Experimental data showed that 2-hour tempering at any temperature does not provide the required combination of strength and toughness, though the results of tempering at 750°C are the closest to it. Attempts to use double tempering at 750°C were successful only in several cases. This is probably due to the fact that, as dilatometric study showed, at 750°C austenite formation started and proceeded in an isothermal mechanism, i.e. the amount of austenite increased with increasing holding time. If one interrupts holding and cools the specimen down, then a part of austenite that formed during holding transforms to martensite. Thus, the first tempering is actually an intercritical quench hardening operation. So, in the second part of the study the intercritical quench hardening was consciously performed by varying the temperature of the first tempering from 750°C to 800°C and decreasing the temperature of the second one to 700°C (holding 2 hours, air cooling) in order to eliminate the strengthening effect of fresh martensite. Results showed that plasticity δ increases and strength properties decrease steadily with increasing temperature of intercritical quenching. The values of KCV^{-60} are very high and increase with increasing the temperature of heating in the intercritical range. This effect is mostly due to continuing high-temperature tempering of martensite that had not transformed to austenite, though precipitation and coalescence of carbide particles may play some role, too. However, in this series of experiments the required combination of mechanical properties was not achieved either. It became evident that the temperature of the second tempering of 680–700°C is too high, but now because of a great decrease in yield and ultimate tensile strength of a part of prior martensite that transformed to austenite during the first tempering and then to fresh martensite during austenite cooling lower M_s. The strength of this part of martensite is higher than that of prior martensite tempered in the intercritical temperature range, at any temperature of the second tempering. Thus, the increase of the temperature of the first tempering increases final impact toughness, while the decrease of the temperature of the second tempering increases strength characteristics. The choice of temperatures of both temperings is a multivariant search that requires vast research. We tried only one additional mode, when tempering temperatures were taken as 765°C and 635°C. This provided the required level of mechanical properties with some extra impact toughness, which may be important for massive parts.

Keywords: 13Kh12N2W2MF steel; intercritical quench hardening; tempering; strength; impact toughness.

Introduction

The steel grade 13Kh11N2W2MF was developed as a high-alloy chromium heat-resistant martensitic class steel for exploitation at temperatures up to 600 °C [1]. However mechanical engineers started to use this steel for critical parts of oil pumps, valves and other locking devives of oil pipelines due to its good corrosion resistance, high strength and significant impact toughness at negative temperatures. Technical requirements for steels of this class include resistance to corrosion, V-notch impact toughness at –60 °C (KCV^{-60}) greater than

24.6 J/cm^2 and yield and ultimate tensile strength ($\sigma_{0.2}$ and σ_b) not less than 650 and 800 MPa, respectively. A difficulty in providing these requirements is that the parts vary in size, and cooling rate after high-temperature tempering differs in a rather wide range. Slow cooling of massive parts made of high-chromium steels may cause temper embrittlement [2, 3] accompanied by carbide precipitation, which decreases the impact toughness sharply. The engineers of a «Konor» company (Chelyabinsk) have faced this phenomenon. Finishing heat treatment at that enterprise was quench hardening and 6-hour tempering at 750 °C with subsequent air or oil cooling. However, stable combination of required levels of impact toughness and strength failed to be achieved. Experiments with double tempering at the same temperature did not yield positive results either. So it became necessary to develop a special heat treatment schedule of 13Kh11N2W2MF steel. It is the main issue of this work. At the first stages of research a problem of lacking information on critical points of this steel appeared; our study of this problem was published in paper [4].

Materials and Methods

Standard specimens for tensile and impact tests were turned from billets cut from a forging previously normalized after 2-hour holding at 980 °C. Chemical composition of the steel is shown in **Table 1**.

First, the effect of tempering temperature on room temperature mechanical properties of the steel was studied in order to reveal the tendencies of change of principal characteristics. Tensile properties measured with INSTRON 5882 tensile testing machine at tension rate of 5 mm/min are shown in **Table 2**. Impact toughness tests were performed with IO 5003-0.3-12 impact pendulum-type testing machine and are shown in **Table 3**. The general character of strength, plasticity and toughness change is typical for alloy steels [5]. Of special interest is the temperature range about 475 °C where a small maximum of strength and minimum of impact toughness is observed. Classical “475-degree brittleness” cannot develop at 11 %Cr [6], so the reasons of embrittlement are probably precipitation of carbides and phosphorus segregation at prior austenite grain boundaries.

Analysis of Tables 2 and 3 permits to conclude that no one of the tempering regimes used permits to attain the required combination of mechanical properties, the results of tempering at 750 °C being the most close to it. Engineers of the Konar company attempted to raise impact toughness by means of double tempering at 750 °C, and in several cases this result was achieved. However, in most experiments the unallowable scatter of impact toughness among specimens subjected to the same heat treatment was observed. This was probably due to the following circumstances.

Table 1

Chemical composition of the 13Kh11N2W2MF steel, wt. %

C	Si	Mn	Cr	Ni	W
0.144	0.60	0.23	10.8	1.50	1.86
Mo	V	Cu	S	P	
0.37	0.29	0.13	0.005	0.005	

Table 2

Tensile properties of the 13Kh11N2W2MF steel after tempering at different temperatures T_{temp} (measurements at room temperature)

T_{temp}, °C	$\sigma_{0.2}$, MPa	σ_b, MPa	δ_5, %	ψ, %
200	1360	1570	11.3	54.7
400	1358	1536	12.1	53.9
450	1394	1510	12.1	53.7
475	1436	1550	12.0	53.1
500	1186	1370	13.8	59.3
550	1056	1210	14.7	60.7
600	940	1039	15.5	61.2
700	724	837	18.3	65.8
750	630	793	22.3	66.1

Table 3

U-notch impact toughness (KCU) and Brinell hardness (HB) of the 13Kh11N2W2MF steel after tempering at different temperatures (measurements at room temperature)

T_{temp}, °C	KCU, J/cm^2	HB
200	60.1	442
400	59.0	439
450	52.1	436
475	37.6	447
500	72.5	390
550	86.2	346
600	102.1	318
700	133.0	249
750	160.0*	236

* KCV^{-60} = 24.1 J/cm^2

Fig. 1 shows dilatograms of two specimens heated to 980 and 750 °C and cooled. The dilatogram of the specimen heated to 980 °C at 30 deg/min does not show any effects near 750 °C. For the second specimen, one sees first a bending, and then abrupt but small lowering of the curve. On subsequent cooling the curve proceeds lower, at almost constant distance from the heating curve. Near 410°C a new bending occurs, after which the curve approaches the initial one. These phenomena have an unambiguous explanation. At 750°C austenite formation starts; it occurs as isothermal, i.e. the amount of austenite formed increases with increasing holidng time. It follows from the growing hardness of specimens held at 750°C for different time and water cooled (**Fig. 2**).

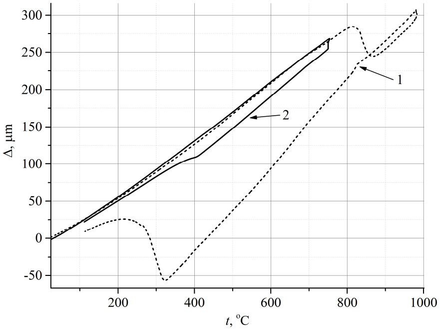

Fig. 1. Dilatograms of heating of specimens to 980 (1) and 750 °C (2), holding and cooling

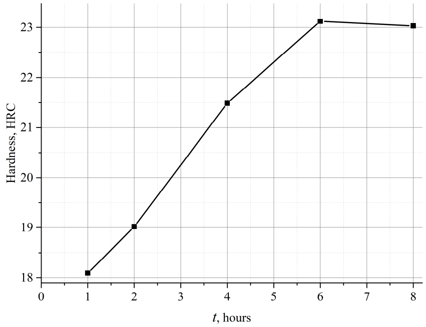

Fig. 2. Effect of holding time at 750 °C on steel hardness after cooling

If the holding is interrupted and the specimen cooled, then the portion of austenite already formed transforms to martensite near 410°C. Consequently, austenite formation and its transformation to martensite occurs both in the first and in the second tempering at 750°C. The martensite formed at the final stage of heat treatment is untempered and will of course increase hardness and decrease impact toughness of steel. Actually, any heating to 750°C is a mixed treatment, i.e. tempering + intercritical quenching (during cooling after the second tempering). To exclude martensite formation, the second tempering is to be performed at temperatures lower than 750°C.

Taking into account the results of investigation [5], we thus realized consciously the intercritical quenching, raising the temperature of the first tempering-quenching stepwise from 750 to 800°C. The temperature of the second tempering was chosen lower than 750°C but high enough (700°C, holding 2 hours, air cooling) to decrease the strengthening effect of martensite. Only in one of the regimes tried the second tempering temperature was lowered to 680 °C (see **Table 4**).

Table 4

Mechanical properties of the 13Kh11N2W2MF steel after double tempering

No.	Tempering temperature, °C*		$\sigma_{0.2}$, MPa	σ_b, MPa	δ, %	KCV^{-60}, J/cm^2
	1st	2nd				
0	750	700	626.1	759.3	24.8	51.7
1	765	700	548.6	732.0	26.4	67.4
2	765	680	526.0	729.5	27.3	65.1
3	780	700	509.0	717.5	27.8	67.7
4	800	700	483.0	710.5	27.8	69.2
5d	765	630	651.9	807.0	22.9	54.8

* Tempering time 2 hours in all cases

Experimental results show that plasticity (ultimate elongation δ) increases and strength properties decrease steadily with increasing temperature of the first tempering (intercritical quenching) in the range of 750–800°C. As for impact toughness KCV^{-60}, the use of intercritical quenching with subsequent tempering below Ac_1 makes it very high, and increasing with the increase of intercritical quenching temperature. To explain such behaviour one must take into account ght fact that when the steel is heated to intercritical temperature range, prior martensite is separated into two parts. One part remains α phase, i.e. prior martensite subjected to very high temperature tempering, has lost its increased dislocation density, martensite substructure and a large amount of dissolved carbon, according to the phase diagram [5]. These processes, as well as coalescnence of carbides, result in softening of this part of specimen volume, increasing plastiticity and impact toughness, the greater the higher is the heating tempearture in the intercritical range. Another part of prior martensite transforms first to austenite, and on further cooling to fresh martensite with high dislocation density and, supposedly, with higher carbon concentration. The strength of this part of martensite increases steadily with decreasing temperature of the second tempering due to retaining greater amount of defects and carbon atoms in its lattice. So, increasing temperature of the first tempering (quenching) increases resulting impact toughness of steel, while dcreasing temperature and duration of the second tempering increases its strength.

Let us apply these considerations to the data on mechanical properties of heat treated steel in Table 4 (excluding the sample 5d). Increasing the temperature of the first tempering (intercritical quenching) in no case yielded the required combination of mechanical properties, in spite of very high impact toughness obtained in all regimes. Evidently, the temperature of the second tempering of 680–700°Cwas too high again, but now because of very great decrease of ultimate and proof strength of the part of prior martensite that is retained during holding in the intercritical temperature range. That is, the choice of temperatures of the first and the second tempering is a multivariant search that requires vast investigation. We limited ourselves to one additional regime 5d (**Table 4**), where the first tempering was done at 765, and the second at 635 °C (duration 2 hours in both cases). The obtained values of mechanical properties satisfy the requirements, and there is some extra impact toughness which may be important for massive components. In conclusion it should be noted that for clear understanding of the processes in all detail one needs to study thoroughly the character of precipitation and dissolution of carbides during the treatments.

Conclusion

1. Austenite formation on heating of 13Kh11N2W2MF steel starts isothermally somewhat below 750°C.

2. The levels of meachanical properties of the steel required by technical conditions for locking devices of pipelines cannot be provided by any combination of quench hardening and single tempering, even at a temperature as high as 750°C.

3. Optimal regime of finishing heat treatment is double tempering, the first stage being actually an intercritical quench hardening. It is shown that increasing the temperature of the first tempering increases significantly final impact toughness, while decreasing the temperature of the second one increases steel strength.

4. Results demonstrate that there may be many variants of tempering regimes that would provide required combination of strength and toughness of steel. One of such regimes tried in this research is double two-hour tempering at 775 and then at 635°C.

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ВЛИЯНИЕ МЕЖКРИТИЧЕСКОЙ ЗАКАЛКИ НА МЕХАНИЧЕСКИЕ СВОЙСТВА СТАЛИ 13Х11Н2В2МФ

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Аннотация. Статья посвящена изучению возможности использования корозионностойкой и жаропрочной стали 13Х12Н2В2МФ для изготовления запорной арматуры и деталей нефтяных насосов. Технические условия для сталей этого класса сводятся к требованию стойкости по отношению к коррозии и уровней ударной вязкости KCV при –60°C более 24,6 Дж/см^2, а также пределов текучести и прочности более 650 и 800 МПа соответственно. Сложность ситуации заключается в том, что изготавливаемые детали могут иметь разную массу, поэтому для них скорость охлаждения от температур высокого отпуска после закалки изменяется в довольно широких пределах. При замедленном охлаждении массивных деталей из высокохромистых сталей может возникнуть обратимая отпускная хрупкость, усиленная выделениями карбидной фазы, что резко понижает ударную вязкость. В первой части исследования была поставлена цель выяснить влияние температуры отпуска на механические свойства стали при комнатной температуре. Анализ полученных данных позволил заключить, что ни при одной температуре двухчасового отпуска не удаётся достигнуть требуемого сочетания механических свойств, хотя результаты для отпуска при 750 °C максимально близки к нему. Попытки использовать двукратный отпуск при 750°C оказывались успешными только в отдельных случаях, что произошло, вероятно, в силу следующих причин. Как показала дилатометрия, при 750°C начинается образование аустенита, которое идет по изотермическому варианту, то есть количество образующегося аустенита возрастает по мере повышения длительности выдержки. Если прекратить выдержку и провести охлаждение, то возникшая порция аустенита превращается в мартенсит. Следовательно, первый отпуск фактически является межкритической закалкой. Поэтому во второй части исследования была сознательно реализована межкритическая закалка образцов при температурах первого отпуска от 750 до 800°C, причем температура второго отпуска была снижена до 700°C (выдержка 2 ч, воздух), чтобы убрать упрочняющий эффект от свежего мартенсита. Результаты экспериментов показали, что с повышением температуры межкритической закалки величина δ (пластичность) непрерывно возрастает, а прочностные свойства снижаются. Значения KCV^{-60} оказываются очень высокими, причём увеличиваются с повышением температуры в межкритическом интервале. Этот эффект в основном связан с продолжающимся высоким отпуском не превратившегося в аустенит мартенсита, хотя выделение и коагуляция карбидных частиц могут оказать некоторое влияние. Однако требуемого сочетания механических свойств и в этих опытах достигнуто не было. Стало очевидным, что температура второго отпуска 680–700°C оказалась завышенной, но теперь по причине очень сильного снижения пределов прочности и текучести у той доли исходного мартенсита, которая в ходе первого отпуска превращается сначала в аустенит, а после охлаждения последнего ниже точки M$_s$ – в свежий мартенсит. Его прочность при любой температуре отпуска выше, чем у исходного мартенсита, отпущенного при температурах межкритического интервала. Итак, повышение температуры первого отпуска повышает конечную ударную вязкость, тогда как снижение температуры второго отпуска увеличивает свойства прочности. Выбор температур первого и второго отпуска является многовариантным поиском, требующим обширных исследований. Мы ограничились одним дополнительным режимом, согласно которому температура первого отпуска была принята равной 765, а второго 635°C. Достигнутые величины механических свойств удовлетворяют требованиям к изделиям, причём имеется запас по ударной вязкости, который важен для массивных деталей.

Ключевые слова: сталь 13Х12Н2В2МФ; межкритическая закалка; отпуск; прочность; ударная вязкость.

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