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Phase Composition of TRIP-Steels after Aging

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Abstract.
The aim of the present study is to investigate the influence of various elements (carbon, nitrogen, manganese and chromium) on the phase composition after aging of four carbon and nitrogen austenitic-unstable TRIP-manganese and chromium-manganese steels. The results showed that: after aging, manganese austenitic-unstable steels, both carbon and nitrogen, form chemical compounds that destabilize austenitie and particularly transformed into martensite. When aging, chromium-manganese austenitic steels do not form martensite but only produce nitride or carbonitride phases. In the process of aging of carbon austenite, mixed carbides of cementite type and of the type $Me_{23}C_6$ are released.

Keywords: phase composition, aging, TRIP-steels, XRD.

1. Introduction

Austenitic-unstable steels are group of steels characterized in that the deformation and the thermal treatment sharply change their phase composition. After quenching, they have a virtually austenitic structure. When cooling to sub-zero temperatures, the steels form the so-called thermal martensite, at low degrees of deformation epsilon-martensite is obtained, and at higher degrees of deformation – deformational martensite.
These properties are mainly due to their balanced chemical composition. In austenitic – unstable steels, the aging processes have a major impact on their tendency towards martensite formation in thermal and deformation influence. The formation of new phases during aging is due to the presence of carbide and nitride-forming elements in the solid solution, stabilizing of the austenite and formation of martensite at temperatures above room temperature.
Aim of the present work is to investigate the influence of the different elements (carbon, nitrogen, manganese and chromium) on the phase composition after aging in four carbon and nitrogen austenite- unstable manganese and chromium- manganese steels.

2. Materials and methods

The object of the study is four austenitic-unstable steels of chemical composition, shown in **Table 1**.

Table 1. Chemical composition – wt. %

Steel	C%	N%	Mn%	Cr%
X30Mn12	0,32	-	12,42	-
XA25Mn	0,04	0,246	12,84	-
X30CrMn10.10	0,37	-	10,43	10,73
X20A20CrMn10.10	0,22	0,237	10,77	10,56

The above compositions are selected from austenitic – unstable steels which after quenching have a virtually austenitic structure and show a good propensity for martensitic deformation.
Test specimens of the investigated steels are preliminarily quenched from a temperature of 1150 ° C in water. Aging is carried out for two hours at 800 °C, where previous studies have shown that the aging processes are most intense.
The samples tested were pretreated in a H_2SO_4 solution to purify from the oxide coating preventing the identification of the carbide and nitride phases. The thus-cleaned samples are subjected to electrolytic dissolution in a salt-acid solution at a current density of 0,05A/cм^2 after which X-ray phase analysis (XRD) was performed on the treated anode sludge.

3. Experimental results and discussion

X-ray diffraction studies of solid samples and extracted anode sludge showed the following results – **Table 2:**

Table 2. Results of X-Ray analysis

Steel	Phase composition after quenching	Phase composition after aging
X30Mn12	austenite+5% martensite	austenite+15% martensite
XA25Mn	austenite+10% martensite	austenite+30% martensite
X30CrMn10.10	austenite	austenite+$(Cr,Mn)_{23}C_6$ + $(Fe,Mn)_3C$
X20A20CrMn10.10	austenite	austenite+Mn_5C_2+Cr_2N

The experimental curves obtained on the "Леко TN-314" apparatus from the quantitative nitrogen assay in the anode sludge of samples of the nitrogen-alloyed alloys – XA25Mn and X20A20CrMn10.10 are shown in **Fig.1.**

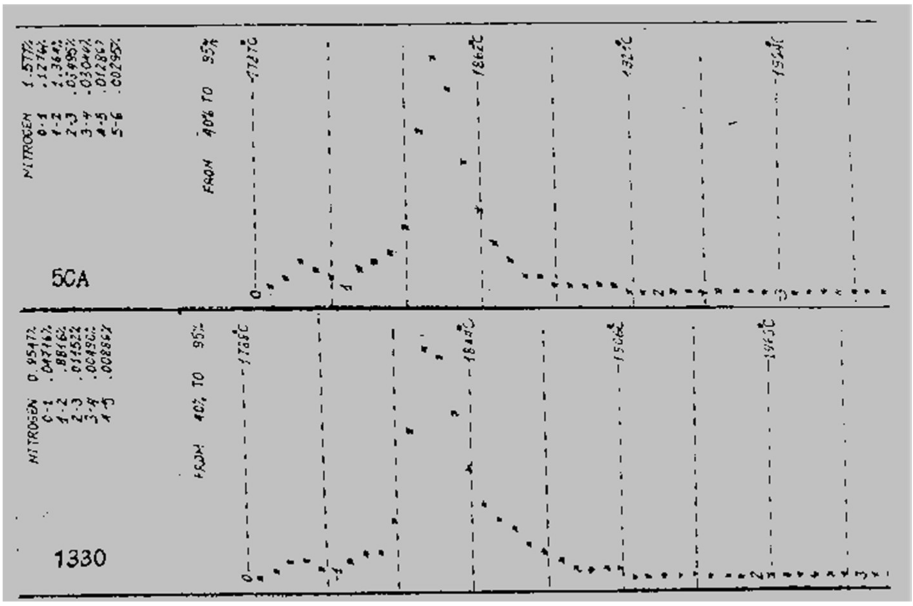

Fig.1. Experimental decomposition results of Leko TN-314 nitrides [5]

The heating temperature is recorded in the abscissa, and the ordinate is the amount of nitrogen released at the respective temperature. The apparatus allows automatic recording of the set sum values of the quantities of nitrogen evaporated at the appropriate temperature intervals from decomposition of the available nitride or carbonitride phases as well as the total amount of nitrogen in the entire sludge. The results are shown in **Table 3.**

Table 3. Results from the quantitative analysis of nitrogen sludge

Alloy designation	Nitrogen content in the sample %	Nitrogen content (in wt%) in anode sludge	Nitrogen content (in mass%) in the maximum
XA25Mn	0,246	1,577	1,36
X20A20CrMn10.10	0,190	0,95	0,88

As it can be seen from the experimental results, the XRD analysis shows that in nitrogen and carbon steels alloyed with manganese only, no evidence of carbide or nitride phase presence is observed after aging. Undoubtedly, the processes of aging in these steels have occurred, as destabilization of austenite occurs from the release of manganese from the solid solution, the formation of new phases, and the transformation of part of austenite into martensite. Furthermore, there is a nitride phase in XA25Mn which is demonstrated by the thermal curve of "Леко TN314" in **Fig.1,** where the maximum of the manganese nitride alone is clearly outlined. Probably this is stable Mn_3N_2, as the presence of this nitride is found in our other studies in steels with similar compositions [1, 2]. Stoichiometric studies show that, with the available nitrogen content in the XA25Mn melt, provided that all of the nitrogen is bound in manganese nitride, the total nitride content cannot exceed 1.56% by mass, which cannot be detected by the XRD method. Similar calculations for the carbon alloy show the presence of, for example, Mn_5C_2, of not more than 2.8% by weight, which is also difficult to be detected by XRD method.
The larger amount of martensite formed in the nitrogen-alloy after aging is due to the fact that nitrogen austenite has a lower stacking fault energy (SFE) compared to that of the carbon austenite and from there they are more prone to martensite formation [3].
XRD analysis of alloys containing 10% of chromium shows that austenite remains stable and does not form thermal martensite when aging, and from it phases typical of chromium-manganese austenitic steels are formed- **Table 2.**
Carbon austenite (X20A20CrMn10.10) after aging forms both types carbides- $(Cr,Mn)_{23}C_6$ and $(Fe,Mn)_3C$. It is known that manganese, as well as chromium, can replace a significant amount of the iron atoms in the cementite and the solubility of the alloying element in the cementite is as large as the closer it is to the iron in the periodic table of the elements [4].
The presence of Mn_5C_2 and Cr_2N is observed in the nitrogen-alloyed chromium-manganese austenitic-unstable steel- X20A20CrMn10.10. The presence of only one nitride Cr_2N is also confirmed by the nitrogen maximum of the thermal decomposition curve in **Fig.1**. This, of course, is easily explained, knowing that nitrogen is preferentially bonded to Cr in the C, Mn, Cr, Fe system i.e. the affinity of nitrogen in the direction of Cr, Mn, and Fe decreases [5]. The difference in the thermodynamic potential of Cr2N and that of manganese nitride at the aging temperature which for Cr_2N is (-12,12 kcal/mol), and for Mn_3N_2 is (-9,17 kcal/mol) is very small [6] as it can be seen on **Fig.2.**

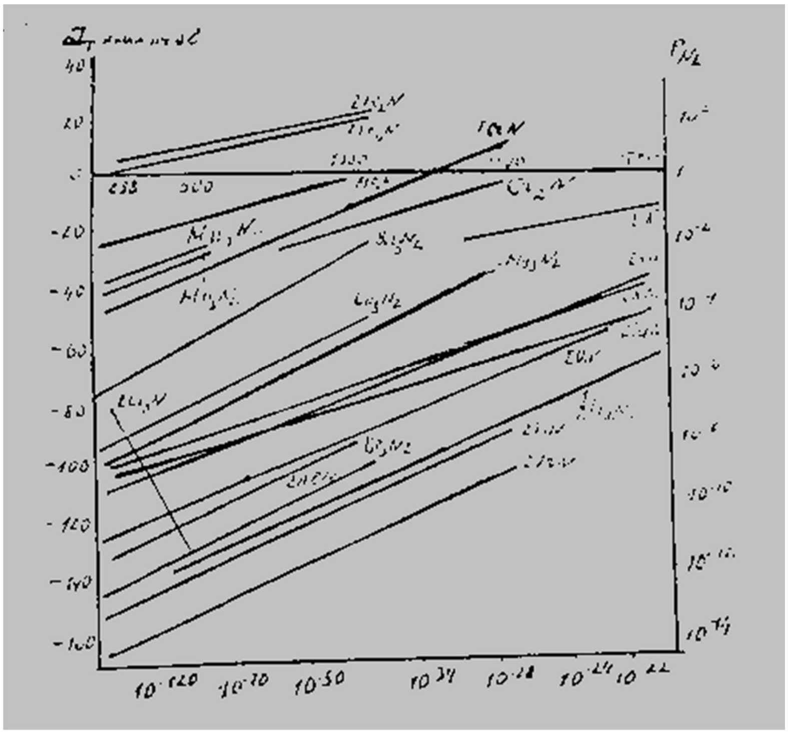

Fig.2. Temperature dependence of the isobar-isothermal nitride formation potential [5]

4. Conclusions

1. Upon aging, manganese the austenitic-unstable steels, both carbon and nitrogen- alloyed, form compounds that destabilize austenite, and it is partially transformed into martensite. This destabilization is significantly greater in the nitrogen austenite, which has a lower stacking fault energy (SFE) than that of the carbon one.
2. On aging, chromium-manganese austenitic steels do not form martensite but release nitride or carbonitride phases.
3. In the process of aging of carbon austenite, mixed carbides of cementite type and of the type $Me_{23}C_6$ are formed.

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