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STRUCTURE AND PROPERTIES OF MA-STEEL WITH RARE- EARTH ELEMENTS ADDITION

WPŁYW DODATKÓW METALI ZIEM RZADKICH NA STRUKTURĘ I WŁASNOŚCI STALI

Up to now rare earth elements have been used relatively seldom as additions to ferrous alloys. Previously, they were taken interest in because its application was possible to remove harmful sulphur from iron alloys. Added, in small amounts, to the liquid metal in ladle prior to mould pouring, they significantly improved the flowing power of alloy casts and caused significant structure refinement. Rare earth elements as alloy additions can be also successfully applied in order to improve tensile strength and yield strength. RE addition to steels, intended for operation in elevated temperature, accounts for a considerable increase in creep limit and creep strength. Investigation of steels with RE addition and remaining components content resembling that of 10G2VNb demonstrated that yield strength and tensile strength were higher than those presented in the literature for such a steel type. The paper presents selected results of investigations of mechanical properties as well as the results of structural investigations. It also shows the impact of structural heterogeneity, resulting from RE compounds, on steel properties.
Keywords: Rare earth elements, structure, properties

Metale ziem rzadkich (ZR) stosowano dotychczas stosunkowo rzadko jako dodatki do stopów żelaza. W latach ubiegłych interesowano się nimi głównie dlatego, że umożliwiały usuwanie szkodliwej siarki ze stopów żelaza, a dodoawane w niewielkich ilościach do ciekłego metalu w kadzi przed odlaniem do form znacznie polepszały lejność staliw stopowych oraz powodowały znaczne rozdrobnienie struktury. Pierwiastki ziem rzadkich jako dodatki stopowe mogą być z powodzeniem stosowane do podwyższania wytrzymałości na rozciąganie, granicy plastyczności, a jako dodatek do stali przeznaczonych do pracy w podwyższonych temperaturach pozwalają także znacznie zwiększyć granicę pełzania i wytrzymałość na pełzanie. Badania przeprowadzone na stali z dodatkiem ZR o zawartościach pozostałych składników stopowych zbliżonych do składu stali 10G2Nb pokazały, że granica plastyczności oraz wytrzymałości na rozciąganie są wyższe w porównaniu do danych lite-

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raturowych dla tej stali. W niniejszym opracowaniu przedstawiono wybrane wyniki badań uzyskane w przeprowadzonych próbach, a także wyniki badań strukturalnych.

1. Introduction

Rare earth elements comprise 17 elements of lanthanide series and also scandium and yttrium. Lanthanides are usually divided into two groups:

- light lanthanides (from lanthanum to europium)
- heavy lanthanides (from gadolinium to lutetium)

According to the present state of knowledge of the Earth natural resources, it is estimated that at the current level of demand for them, they will be still available over at least the next thousand years. The largest deposits of rare earth elements are found in China, Russia, the USA, Australia, India and Vietnam [1, 2]. At least 200 minerals containing rare earth elements are known to exist at present.

Materials containing mixtures of rare earth elements are applied to many industries, e.g. metallurgy, optical equipment manufacturing, electronics and refineries.

2. Re applications to metallurgy and foundry

Cerium mixtures, called mischmetal, are used in metallurgy. They are alloys, in which the dominant element cerium, amounts to approx. 50%, others are lanthanum, usually not exceeding 20% and small amounts of neodymium and praseodymium as well as trace amounts of iron and silicon. The mischmetal most often used in Poland so far has the following chemical composition: cerium, approx. 49%, lanthanum — 21%, neodymium — 20%, praseodymium — 8.5% the remaining components are iron, magnesium, aluminium and silicon [3, 4, 5].

Rare earth elements demonstrate ideal solubility in liquid steel whereas their solubility in solid state is limited. Too high addition of rare earth elements, exceeding the values necessary for liquid metal treatment (e.g. deoxidation, desulfurisation) results in segregation towards boundaries of primary grains, where low-melting eutectics are formed. At high concentrations, this can cause problems with hot-shortness in rolling. Melting points for eutectics are 785°C for La-Fe and 641°C for Ce-Fe.

Rare earth metals have high affinity for oxygen and sulphur, so adding them leads to strong deoxidation and desulfurisation of metal bath and the compounds being formed are oxides, sulfides and oxysulfides. Due to high RE affinity for oxygen and sulphur and high temperatures, the melts of their compounds are thought to be formed just after RE are added to steel. RE oxides, sulfides and oxysulfides are characterised by high density, therefore it is extremely difficult to remove them from liquid metal. Table presents the properties of selected compounds of rare earth metals with oxygen and sulphur [6]

TABLE

Properties of compounds of RE with O and S [6]

Compound	Melting point, °C	Density, kg/m^3
La_2O_3	~2249	6500
Nd_2O_3	~2271	7300
La_2S_3	~2099	5000
Nd_2S_3	~2199	5400
La_2O_2S	~1993	5800
Nd_2O_2S	~1988	6300

Note that MnS melting point is 1539°C, $Al._2O_3$ — 2030°C, and CaO — 2600°C.

3. Low-alloy steel with re additions

The plates under investigation, 12 mm in thickness, made of steel with rare earth metals additions were manufactured as early as in the 1970s. In those days shipyards demanded large quantities of plates resistant to delamination. The phenomenon results mainly from plastic manganese sulfides being stretched towards working direction. The addition of mischmetal was intended to bind sulphur into brittle and hard sulfides, thus greatly reducing the anisotropy of steels used in shipbuilding. RE additions seem, however, to be of interest again, due to their possible applications to the strengthening of steels, both those working in ambient as well as elevated temperatures. In the 1990s much attention was paid to investigations of steels with vanadium, niobium and nitrogen micro-additions. Owing to creep tests running for many years, it was possible to determine creep strength and creep point in the range up to 30,000 hours. Structural investigations of samples, conducted after creep, demonstrated that the main reason for a dramatic decrease in, e.g. creep strength was coagulation and spheroidisation of the material strengthening phases, i.e. vanadium and niobium carbide nitrides.

The chemical analysis of plate material with RE additions was conducted at the Institute of Ferrous Metallurgy. The chemical composition indicates that mischmetal addition was given to weldable steel of increased strength, with niobium addition, denoted as 15G2Anb. The steel of this type was commonly used in shipbuilding in the 1970s and the 1980s [7].

The structure observed in optical microscope shows ferrite and pearlite. It also demonstrates clear orientation.

More detailed investigations carried out with a scanning microscope and, on thin foils, with a transmission electron microscope, revealed a number of structure peculiarities. It is observed, among others, that on grain boundaries there are precipitates identified as niobium carbide nitrides. At many sites, there are scattered fine particles of diversified sizes, identified as rare earth metals compounds with sulphur and oxygen. In the literature on the subject, they are described as RE oxysulfides.

The size of particles rich in RE elements is very diversified and ranges from several to a few hundred nanometers. Particles of smaller size are difficult to identify with respect to chemical composition. The spectral analysis of precipitates reveals their complex composition. It also shows that RE metals, sulphur, oxygen and iron are their main components. In Fig. 1, one can see steel structure observed in a scanning microscope, with numerous oxysulfide precipitation diversified in size.

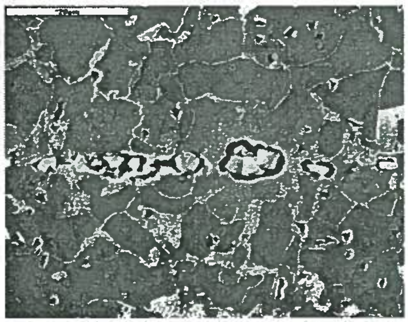

Fig. 1. Steel structure with two visible large precipitates of RE oxysulfides

The precipitate composition was obtained on the basis of spectral analysis with the use of a probe microanalyser: Ce — 26.81%, La — 9.21%, Nd — 6.26%, Pr — 2.69%, S — 42.69%, O — 6.56%, Fe — 5.79%.

In order to estimate the degree of dispersion of RE compounds with sulphur and oxygen, a mapping of the selected area was also performed with the use of a scanning microscope. The result obtained is shown in the photo in Fig. 2. There are visible characteristic bands of particles rich in sulphur.

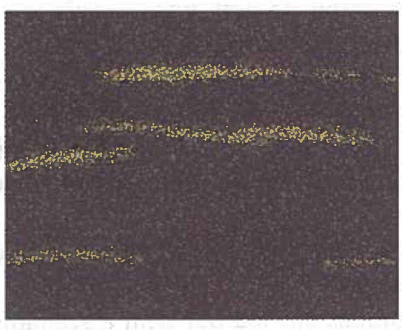

Fig. 2. View of the distribution of particles rich in sulphur. Magnified ×1000

On the basis of microscope observations, it was found out that the majority of dispersive particles have got characteristic angular shape. The data available in the literature, including those concerning the high melting point of individual sulfides and oxysulfides (Table 1), indicate we might expect that in the temperature range of rheological experiments conducted so far for 10G2VNb steels, the RE compounds particles will be stable and will not undergo coagulation or spheroidisation.

Before creep tests started, the properties of steel with RE additions were specified and the results obtained were as follows: at temperature 20°C Rm = 585MPa, Re = 451MPa and at 500°C Rm = 332MPa, Re = 205MPa. At ambient temperature steel shows high ductility, that is A = 33% and Z = 69%.

The properties of the steel under consideration, compared with those of 10G2VNb steel, are lower at ambient temperature and comparable at 500°C (at ambient temperature, 10G2VNb steel shows the following properties: Rm ~ 600–700 MPa, Re ~ 450–600MPa [8]).

In creep tests conducted at 500?C under diversified stresses, the results obtained for the investigated steel show that both creep strength and creep point are higher by no less than 15% when compared with 10G2VNb steel characteristics.

4. Conclusions

Experimental works carried on steel with the addition of RE metals demonstrate that no plastic manganese sulfides, characteristic of different steels, occur in the structure. The sulphur was totally bound into complex chemical compounds with oxygen and RE metals. Plastic working caused the break-up and dispersion of oxysulfides in the structure. On the basis of the results obtained so far the following conclusions can be drawn:

- at "set" content of sulphur and RE metals in a steel with niobium, the extent to which oxysulfides affect the properties of the steel at ambient temperature is small
- high yield point at 500°C might result from the effect, manifested already at this temperature, of fine oxysulfides particles which occur and are dispersed in the structure
- high, in comparison with10G2VNb, creep point and creep strength at the temperature at which short term creep tests were conducted, indicate that RE oxysulfides might significantly contribute to the increase in those properties
- after obtaining respectively high dispersion in the steel matrix, sulphur compounds with RE can become a strengthening agent

In order to fully estimate the impact of RE additions on the structure and properties of steels in a wide temperature range it is necessary to conduct extensive research into steels of different contents of sulphur and RE metals.

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