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THE ROLE OF CERIUM AS RARE EARTH ELEMENT AT ONE HOT WORK TOOL STEEL

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Abstract: Only a few of rare earth elements (REEs) could be found at tool steels for hot deforming, but their properties and (dis)advantages still are not well known to many consumers. Tool **s**teels always have had a crucial role in various mechanical engineering production methods, either in casting, cutting or deforming processes. In spite of that, the new production methods and further the properties of such obtained tool steels are not well known to many tool designers & technologists. A lot of tool steel grades are renewed, approximately about 60% of total steel number is changed or improved just in last two decades. Modern mechanical engineering could not be image without qualitative tool steels. The new production methods usually bring up a more advanced steel properties. The enlarged hardenability and wear resistance are typical demands from the every tool steel, no matter what for is particular tool steel used, commonly in cutting or deforming processes. It is always expected that such steel possess the pretty low level of non–metallic inclusions, and those levels could be obtainable only by using a specific refining processes during steel making. The most known new processes of tool steel making here are explained on the comprehensive level to the tool designers and other mechanical engineers, evolved in the choosing the most desirable tool steel. Here will be shown why cerium is one of desirable elements in a kind of tool steel for hot extrusion.
Keywords: tool steel, production & refining methods, cerium, tool cleanness

1. INTRODUCTION

The contemporary mechanical engineering could not be image without qualitative tools and materials. It is considered that about 60% of total tool steel number is changed in last two decades. Such miracle changes were provided by many efforts in processing of tool steels. The advanced method of producing the qualitative tool steels offer better properties in comparison to older types of steels. Some methods of steel melting or refining are the warranty for improved to many tool designers or consumers.

The enlarged hardenability and wear resistance are typical demands from every tool steel, no matter what kind of steel is used (for casting, cutting or deforming).The large number of production methods were involved in technology of refining during steel melting.

The refining of the melt is the essential step in the production schedule [1,2]. The way of refining (under the protective atmosphere, method of degasing, vacuum threating, melting under the slag, double or triple remelting, etc.) often is emphasized even in the offer for sale. From that point of view, here is shown one contemporary method used in tool steel production, which is interesting for mechanical engineers and other as users of tools.

Many steels for hot working tools contain main alloying elements, such as Cr, W, Mo and V, but not cerium [3–5]. Here will be analysed the presence of cerium at one steel for a hot working tool, used for extrusion of copper, as one heavy thermal and mechanical loaded tool.

2. PRINCIPAL USAGE OF REEs

Rare Earth Elements (REEs) are used in many devices, in past decades an explosion in demands for these elements and their alloys has happened. Only twenty years ago there were small number of cell phones in use, however, but today the estimation about the number of these phones is over 7 billion. Alloys used for rechargeable batteries in phones or portable computers, in

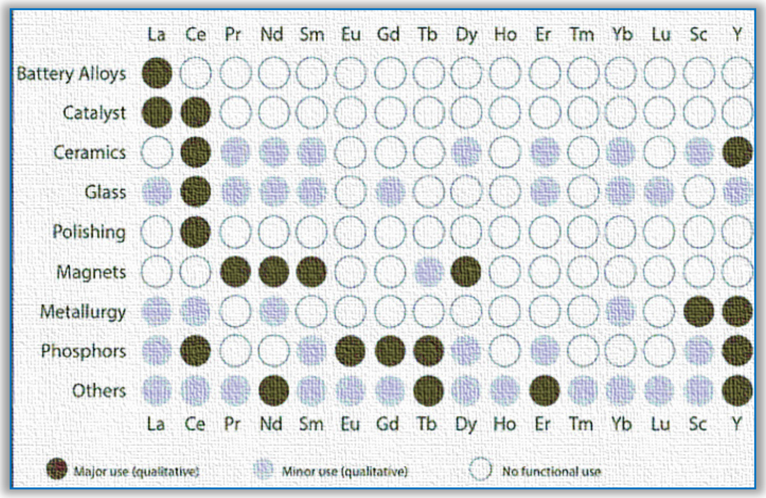

Figure 1. Distribution of REEs for various usage

memory devices, and as catalyst in electric vehicle or hybrid–electric vehicle are produced from REEs, as shown in Figure 1.

The use of REEs metals in metallurgy processes for production of various alloys varies from 7 to 20%, depending from the time and/or country. Materials as glass, marble, granite and other gemstones are often polished with cerium oxide powder.

The REEs are not really rare in content: in the Earth's crust many other valuable elements are much more abundant, for example cerium is 15000 times more abundant than gold.

3. CERIUM IN STEEL

Cerium is silvery–white metal, on air fast becomes dark, pretty soft – only ≈30HB, lighter than iron– density is ρ=6,79g/cm^3, and melts at pretty low temperature – at 795^{0}C. REEs atracted great inte rest in order to understand the their role in both structural or tool steels, no matter that the solubility of almost REEs in solidified iron is pretty low, while in Fe melt they are completely dissolved. Cerium with iron makes an eutection reactin which melts at temperature less than 600^{0}C, see diagram at Figure 2. In spite of such low solubility cerium attracted interest in production of qualitative steels, no matter that in system Fe–Ce there is no any strong phase.

It is worthy to emphasize that cerium with all interstitial elements or inclusions present in steel is able to make compounds as like: hydrides, oxides, nitrides, sulfides, phosfides or silicides. During chemical reaction of cerium with many elements present in molten steel, the large amount of heat is liberated, it means that those reactions are exothermic.

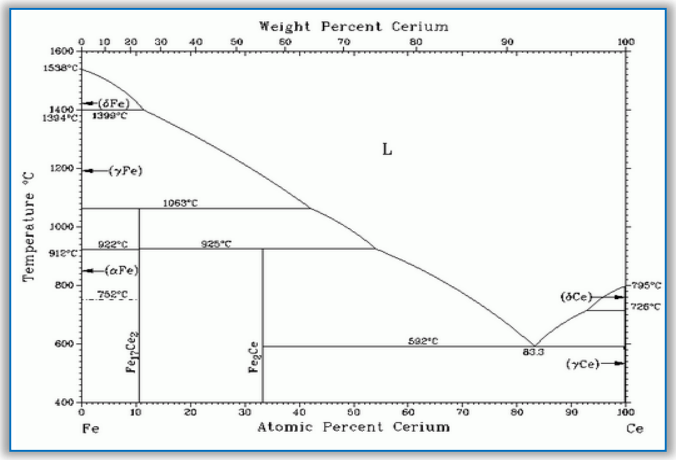

Figure 2. Phase diagram Fe – Ce

According to strong affinity to other elements, especially to non–metal inclusions, cerium may serves for treating a liquid metal, it means for a kind of refining. Cerium is added into molten steel in the form of ferrocerium.

4. INFLUENCE OF REEs ON GRAIN REFINEMENT IN STEEL

It is widely known that microalloying elements (MLE) play an important role in structural steels while in tool steels they have a kind of hidden role in comparison to main alloying elements. The conventional refining of steels, used either for structures or tools, consists of adding the strong carbide elements, frequently Nb, V and Ti [2–6]. The role of REEs in tool steels, either is positive, is hardly known, and from that piont is needed to explain their advantages.

Cerium founds application in producing of nodular iron, for inoculation the structure. After such treating of molten metal with cerium in amounts obout 0,2%, the mechanical properties of solidified metal are increased. Thanks to its high surface activity in melts, cerium is started to apply in producting of qualitative tool steels.

In the periode of steel making, the molten steel generally may be treated either by innoculation for refining the structure just during melting or later after solidification – through the deforming process, when austenite grains are refined (usually by hot rolling). Many production methods were involved in technology for refining the steel microstructure. The refining of the melt is first step in the production schedule of steel. There are developed various ways for refining the melt: under the protective atmosphere, inoculation, way of degasing, vacuum threating, melting under the slag, double or triple remelting, etc. The refining of the melt is one of the most effective method for improving many properties, including the formability of the sheet form. Addition of REEs was applied into structural steels but some producers in past decades introduced one or more from those elements into tool steel. Hot work tool steels are exposed both to high stresses and temperatures during forging/extrusion. Cerium is one element from group of REEs which has shown some useful advantages in such kind of tool steel. Grain refining of solidified steel, when cerium is added, also is recorded in an industrial practice, firstly in structural steels and later in tool steels. Degassing of steel melt withh REEs also is happened, as desired reactions in modification of steel properties.

The effect of modification of solidified structure sometimes is visible nearly by naked eye, in Figure 3 are shown some examples.

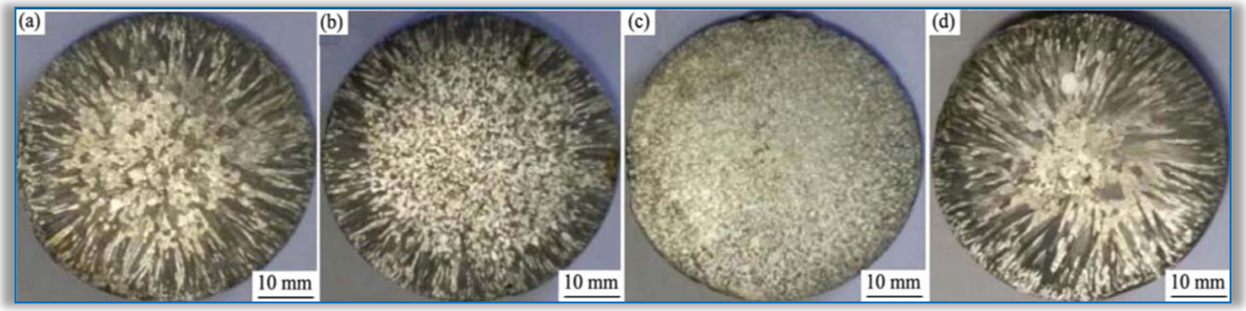

Figure 3. Microstructures of as cast ingot Ø10mm from ferritic stainless steel 434 (ASTM):
a) without Ce; b) with 0,011%; c) with 0,023% and d) with 0,034%Ce [7]

It is evident that a large amount of Ce, Fig. 3d), does not make desired refinement of grain size in steel, just contrary. During solidification, REEs segragete at grain boundaries. Many other REEs also may react with the nitrogen, dissolved in molten steel. Thats why RE elements are worthy for studying.

In the theory of casting but also in practice, is well established that refinement of as–cast structure is an effective method for improving mechanical properties, formability, even the surface appearance of castings. During solidification process of steel, cerium will be rejected from a solid phase and segregate at grain boundaries,

5. CERIUM AND GRAIN SIZE IN CAST H13 TOOL STEEL

In small amounts of cerium [5] up to 0,02% in H13 tool steel, as one represented of steel for working at elevated temperature, has shown the decreasing effect on grain size, but larger amounts of cerium has no further effect on grain size, Figure 4.

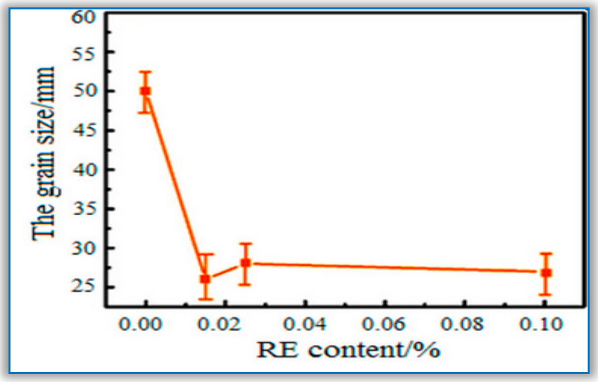

Figure 4. Graing size changes in as–cast H13 steel [8]

Cerium shows the great affinity toward oxygen and sulfur, and melting temperature of formed cerium oxides and sulfides are pretty high, over 1900^{0}C. This fact is importance for understanding the role of cerium oxides or sulfides during crystallization of steel: in structural steels the solidification begins in delta ferrite, phase with the highest melting temperatures. This is way on which cerium acts as a grain refiner on delta phase but not on gamma phase. Such treated tool steel is able to submit the higher loads and working temperatures [4–6], which are far away from atmospheric conditions.

Either the pure cerium posses a pretty low melting temperature, some of the oxides and sulfides of cerium are melting at ≈2500^{0}C. So, cerium is added into molten steel to react with both oxygen and sulfur, making nonmetallic compounds which are less harmful. Further, cerium makes a number of oxides and sulfides. It is established, by XRD or similar analytical techniques, that cerium inclusions (almost as Ce_2O_3 or Ce_2O_2S) will be formed when solidification of treated steel is finished. After treating a molten steel, the ductility (toughness) could be enhanced. This is an important property/ability, either for structural or tool steels.

The shape and size of non–metallic inclusions are changed after cerium addition into molten steel, it means that cerium acts as grain refiner. Formed inclusions on cerium base are more desirable than for example of mangansulfid (MnS). In many structural steels the MnS is an obvious nonmetallic inclusion [8]. It implies on imrpoving the ductility of such treated steel. Cerium–sulfur phase diagram still is not well investigated. Cerium with sulfur makes four compounds:CeS, Ce_3S_4, Ce_2S_3 and CeS_2, from left to right in Figure 5.

ISSN 1584 – 2665 (printed version); ISSN 2601 – 2332 (online); ISSN-L 1584 – 2665

From various sulfides, the CeSposses the highest melting temperature, see the same diagram. The formed cerium sulfides may further react and form another kind of compound, for example cerium oxysulfides.

Silica is often present as non–metallic inclusion in steels, and cerium oxide may react with it giving the cerium–silicate $Ce_2O_3{\cdot}2SiO_2$. Further, it could be expected that cerium will form inclusions as Ce_2O_2S, when one atom of oxygen is replaced in compound Ce_2O_3. These facts show that the investigation of cerium behavior in molten or solidified steel is pretty complex, and many other disciplines (as X–ray techniques, crystallography, and metallography, mechanical and technological testing, etc.) should be applied.

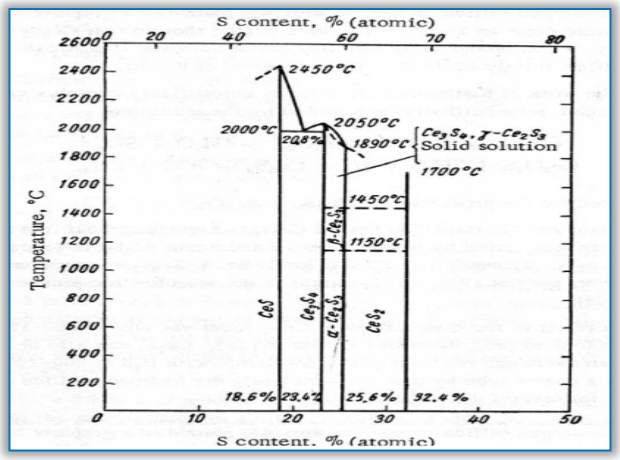

Figure 5. Cerium–sulfur phase diagram (Samsonov 1964)

For classification of nonmetallic inclusions were developed and standardized scales for more precise definition of inclusion type, way of distribution, size, etc. [9,10].

6. CONCLUSION

The servicing life of every tool, in spite of working conditions, markbly is determined by a kind of used steel.

Pure cerium practically is insoluble in iron. Even though cerium posses a pretty low melting temperature (≈800^{0}C), but its oxides and sulfides are melted at pretty higher temperatures, in interval 1900–2500^{0}C. The main role of addition of cerium into the molten steel is first of all to react with oxygen and/or with sulphur.

Thanks to its high surface activity in melts, cerium is started to apply in producting of qualitative tool steels, firstly on the behalf of structure modification/refining. Forming of non–metallic inclusions by adding of cerium in amount ≈0,2% into steel for hot extrusion of copper products, such steel has shown the benefitial effect on tool service life.

This is of importance for exploating the toll steel for hot deforming, but also could be said for other demands or qualitative structural steels.

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Note: This paper was presented at IIZS 2023 – The XIII International Conference on Industrial Engineering and Environmental Protection, organized by Department of Mechanical Engineering and Department of Environmental Protection of the Technical Faculty "Mihajlo Pupin" Zrenjanin, from the University of Novi Sad, in cooperation with partners – University Politehnica Timisoara, Faculty of Engineering, Hunedoara (ROMANIA), University "St. Kliment Ohridski", Technical Faculty, Bitola (MACEDONIA), "Aurel Vlaicu" University of Arad, Faculty Of Engineering, Arad (ROMANIA), University of East Sarajevo, Faculty of Mechanical Engineering East Sarajevo, Sarajevo (BOSNIA & HERZEGOVINA) and University of Giresun, Faculty of Engineering, Giresun (TURKEY) – in Zrenjanin, SERBIA, in 05–06 October, 2023

ISSN 1584 – 2665 (printed version); ISSN 2601 – 2332 (online); ISSN-L 1584 – 2665