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Comparative study of 9% Cr martensitic-ferritic steels using differential scanning calorimetry

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Abstract

9% Cr ferritic-martensitic steels were developed from the seventies with the aim of coping with the requirements put by the use of structural components under compromised service conditions, i.e., elevated temperatures and highly corrosive environments. Those conditions are typical in the operation of thermoelectric power plants with fossil fuel; in addition, in the case of applications of these materials to structural components in advanced nuclear fission and fusion reactors there are strong irradiation fields introducing even more severe restrictions.

In this paper we study comparatively the transformation behavior of three 9% Cr alloys by using the Differential Scanning Calorimetry (DSC) technique, with thermal cycles including heating, austenite holding and cooling at rates between 1.5 and 50 ºC/min. The starting metallurgical state corresponds to the as-received -that is, normalized and tempered- material. Transformation critical temperatures are determined in each case and, in particular, the dependence of those temperatures with respect to the cooling rate is examined. At the same time, approximate bounds of the critical cooling rate for martensite formation are given and compared between the different alloys. Finally, DSC results are evaluated as compared to literature values and to previous results of our laboratory obtained by the dilatometry technique.

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Keywords: Differential scanning calorimeter; 9% Cr Steels; Martensitic transformation; Critical cooling rate

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1. Introduction

Nomenclature

CCT	Continuous Cooling Transformation
TTT	Time-Temperature-Transformation
DSC	Differential Scanning Calorimetry

9% Cr martensitic-ferritic steels have been extensively used in manufacturing components for thermal power plants, boilers, heat exchangers, piping and tubing, etc., due to an excellent combination of properties such as creep resistance, toughness and good performance against oxidation at high temperatures. The continuous improvement of properties of 9% Cr materials has allowed a substantial increment of the target performance: a rise in the service temperature – which means in turn a higher efficiency of thermodynamic cycles- and higher values of rupture strength. From the environmental point of view, a higher efficiency will also mean a reduction of CO_2 emissions. In Argentine, grade P9 materials –containing approximately 9% Cr, 1% Mo and less than 1% Mn, Si and Ni- are used in thermal cracking furnaces in most of the oil refineries in activity. On the other hand, P or T91 materials, which also include Nb and V as alloying elements, are used in structural components of conventional thermal power plants such as heat exchangers, high pressure overheaters, etc.: in whole, there are 43 thermal machines operating under the combined cycle regime and grouped in 21 thermal plants. It must be also pointed out that grade 91 steels are the first option as for candidate materials for structural applications in the next generation of nuclear fission reactors, i.e. Generation IV reactors; besides, in the last 20 years and on the grounds of P or T91-type materials there have been developed the so-called *reduced activation* steels, foreseen for structural applications in the future fusion nuclear reactors.

1.1. Continuous cooling transformations

Continuous Cooling Transformation (CCT) and Time-Temperature-Transformation (TTT) diagrams allow extracting different parameters that characterize the transformation behavior of steels. In particular, from CCT diagrams the values V_m (critical cooling rate for martensite formation) and V_α (critical cooling rate for ferrite formation) can be assessed. For fixed austenitizing conditions, these parameters represent, respectively, the minimum cooling rate to achieve a fully martensitic structure and the maximum cooling rate to obtain a fully ferritic structure. For intermediate cooling rate ranges, in consequence, “duplex” martensite-ferrite structures are obtained.

The hardenability of the steel can be estimated through the study of the parameters V_m and V_α. Both quantities depend on the austenitizing temperature T_A (through the influence of that temperature on the austenitic grain size *G*) and on the chemical composition of the matrix; in particular, on the fraction of alloying elements precipitated *before* the start of the corresponding transformation during cooling. Thus, CCT diagrams account for the change of V_m and V_α as a function of T_A (for a fixed chemical composition) or as a function of the chemical composition (for fixed T_A) (Honeycombe and Bhadeshia (1995); Brachet (1991)).

The previous literature contains reports on 9% Cr steels using the Differential Scanning Calorimetry (DSC) technique. These studies have focused on aspects such as the kinetics of martensitic transformation (Raju et al. (2010)), the energetics of transformations under heating and cooling cycles (Raju et al. (2007)) and specific heat measurements (Raju et al. (2009)), giving information on the continuous heating and cooling processes.

The present work reports results on the transformation behavior of three 9% Cr steels (ASTM A213 T9, ASTM A335 P91 and ASTM A335 P92) obtained in thermal cycles including heating, austenite holding and controlled cooling under fixed austenitizing conditions, paying particular attention to the martensite start temperature M_s.