A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 58 2013 Issue 3
DOI: 10.2478/amm-2013-0066

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GLOBULAR MICROSTRUCTURE FORMATION IN X210CrW12 STEEL FOR SEMI SOLID PROCESSING USING PLASTIC DEFORMATION OR BORON MODIFICATION

ODKSZTAŁCENIE PLASTYCZNE I MODYFIKACJA BOREM JAKO METODY OTRZYMYWANIA MIKROSTRUKTURY GLOBULARNEJ W STALI X210CrW12 W ZAKRESIE STAŁO-CIEKŁYM

Semi-solid processing (SSP) belongs to advance method of forming metal alloys in the solidus-liquidus range. Such technology requires a fine globular microstructure in a semi-solid range, which can be produced by numerous methods. The present paper focuses on two methods of preparation of a globular microstructure in X210CrW12 tool steel as a possible way of preparation of feedstock for thixoforming: hot plastic deformation (SIMA), and modification with boron. DSC analysis allowed to establish the amount of liquid phase fraction vs temperature. Samples were heated up to the semi-solid temperature range – 1230°C, which corresponds to 17% (SIMA) and 30% (modified) of the liquid fraction. Then they were rapidly cooled. The obtained microstructures of samples were investigated for their suitability for SSP. The microstructure of X210CrW12 steel prepared by SIMA shows a globular microstructure with average grain size 57 μm. The samples after modification with 0.08% (weight pct) boron also feature a globular microstructure with the size of 46 μm. The grains possess an austenitic structure and are surrounded by an eutectic mixture.

Keywords: Semi-Solid Processing, thixoforming, X210CrW12 steel, SIMA, modification, globular grains

Formowanie tiksotropowe jest jedną z nowoczesnych metod kształtowania mikrostruktury stopów żelaza w zakresie temperatur solidus−likwidus. W procesie tym wymagany jest globularny kształt ziaren fazy stałej w zakresie stało-ciekłym. W pracy na przykładzie stali X210CrW12 przedstawiono dwie metody przygotowania mikrostruktury tiksotropowej poprzez: odkształcenie plastyczne powyżej temperatury rekrystalizacji (SIMA) oraz modyfikację dodatkiem – 0,08%$_{wag}$ boru. Przeprowadzono analizę DSC w zakresie solidus−likwidus, która umożliwiła wyznaczenie udziału fazy ciekłej w funkcji temperatury. Próbki zostały nagrzane do 1230°C, która odpowiadała 17% fazy ciekłej dla stali X210CrW12 po odkształceniu (SIMA) i 30% w przypadku stali modyfikowanej, a następnie szybko schłodzone w wodzie. Przeprowadzono charakterystykę mikrostruktury w celu oceny jej przydatności do tiksoformowania. Badania potwierdziły, że dla metody przygotowania stopu wyjściowego metodą SIMA występowały globularne ziarna o średniej wielkości 57 μm. W przypadku stali X210CrW12 po modyfikacji dodatkiem boru, również obserwowano sferoidalne ziarna roztworu stałego o rozmiarze 46 μm.

1. Introduction

Semi-Solid Processing (SSP) is one of the modern methods of forming metal alloys in solidus-liquidus range [1]. It is possible thanks to the unique rheological properties of alloys in semi-solid state, such as the decrease of viscosity under shear stress. The factor which enables the thixotropic flow of semi-solid slurry is the globular shape of solid phase surrounded by liquid phase. 20 to 80% liquid phase is require for thixotropic behaviour of metal alloys [2]. Nowadays, rheoforming and thixoforming of Al-based, Zn-based, and Mg-based alloys is commonly applied in the industry [3-5]. In the case of high-melting alloys, such as steel, a lot of restrictions which relate to the mould material, strong oxidation of feedstock, and temperature control [6] should be considered. Viscosity analysis of steel in semi-solid range enables to predict the behaviour of suspension during SSP, which may allow to adjust technological parameters and improve parts quality [7, 8]. High cost of a feedstock manufacturing is also an obstacle to its widespread application [10]. The method of obtaining globular structure in SSM slurry is one of the important technological parameters. Depending on the method employed, a different grain size and a different fraction of the liquid phase are obtained [10, 11]. In the case of X210CrW12 steel, SIMA (Strain Induced and Melting Activated), RAP (Recrystallization and Partial Remelting) or CSS (Cooling Slope System) methods are most commonly used [1, 10, 12]. Another familiar method is the modification in which the heterogeneous nucleation of solid solution grains is used [1]. It is mainly employed in aluminium alloys [13]. In the case of steel often used modifier is boron [14, 15]. Apart from refining the microstructure, it stabilizes austenite, increases hardenability and lowers the temperature of bainitic transformation [18]. The aim of the study is to present the differences in the microstructure of

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X210CrW12 steel depending on feedstock preparation for the thixoforming process. Additionally, the study aims at characterizing the semi-solid range according to Kazakov's criteria [19, 20].

2. Experimental procedure

2.1. Preparing of X210CrW12 feedstock and heating up to semi-solid range

The X210CrW12 tool steel rods produced by Batory Steel Works S.A. were used in the present study. Their chemical composition was: 2.2%C, 10.9%Cr, 0.6%W, 0.5%Si, 0.4%Mn, 85.4%Fe (all in weight pct). The globular microstructure in the investigated alloys was obtained by plastic deformation above temperature of recrystallization (SIMA [19]), or by modifier addition in the liquid state. In the first method commercially available X210CrW12 steel rods were used after being hot rolled at temperature of approximately 1050°C, then annealed at 840°C for 4 hours, and cooled in a furnace. In the second method rods made of X210CrW12 were melted in an inductive furnace and 0.08% of boron was added into the liquid metal. Boron in master alloy Fe15B was added at a temperature of 1580°C. Rods with 40 mm in diameter and 100 mm in height were then cast into a sand mould. They were then cut into 20×20×50mm samples and placed in quartz capsules, from which the air was pumped out and 5×10^{-2} mbar vacuum was obtained. The capsules with X210CrW12 steel samples were placed in a resistance furnace and heated together with the furnace up to 1230°C at a rate of 10°C/min and held at this temperature for 5 minutes. This temperature corresponds to the semi-solid range in X210CrW12 steel. Then the capsule was pulled out of the furnace, broken and rapidly cooled in water.

2.2. Microstructure, calorimetric analysis and mechanical properties

Chemical composition of X210CrW12 steels were determined using emission optical spectrometer JY 10 000 RF JOBIN YVON. The samples for optical microscopy were polished and etched with Nital. Metallographic analysis was carried out using Leica QWIN image analysis program. X-ray investigations of the phase composition were performed using Cu-Ka filtered radiation using Bruker, Phasher – D2 diffractometer. DSC Q600 SDT calorimeter was used to measure the thermal effects during heating at the rate of 10°C/min in argon atmosphere. The samples of 1.5 mm thickness and the 3.5 mm diameter were heated in a corundum crucible (Al_2O_3). Amount of the liquid phase as a function of temperature was determined according to the procedure described by L. Rogal [22]. It was expressed in volume percentage. Hardness measurements (by Vickers method) were carried out using Zwick/ZHU 250 (HV_5).

3. Results and discussion

3.1. Analysis of solidus-liquidus range

Fraction of liquid phase as a function of changing temperature depends on the method of preparation of feedstock intended for semi-solid processing [1, 10]. Figure 1 shows solidus-liquidus temperature range vs. amount of liquid fraction for X210CrW12 steel: hot rolled (solid line) and modified by boron (dashed line). A temperature of 1230°C was marked on the liquid fraction change curve for points A and B, which correspond to steel after plastic deformation (f_L = 30%) and modification (f_L = 17%). Based on the analysis of the curves from Figure 1, a characterization of semi-solid range was performed according to Kazakov's criteria, results of which are presented in Table 1.

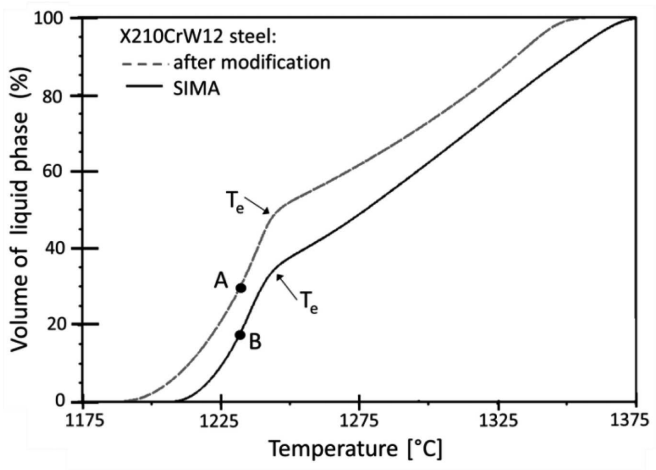

Fig. 1. Liquid fraction curves as a function of temperature for X210CrW12 steel after: hot rolling (solid line), modification (dashed line)

TABLE 1

A characterization of semi-solid range according to Kazakov's criteria for X210CrW12 steel after hot rolling and modification (all percentage are expressed in liquid volume percentage)

State of X210CrW12 steel	T_S	$T_{30\%}$	$T_{50\%}$	T_e	T_L	T_L–T_S	$(df_L/dT)_{30\%}$	$(df_L/dT)_{50\%}$	$\Delta T_{40\%-20\%}$	$\Delta T_{60\%-40\%}$
SIMA	1207	1240	1277	1247	1378	171	0.0131	0.051	22	41
Modified	1184	1230	1246	1243	1354	170	0.0136	0.058	14	33

Significant differences exist in liquid fraction curves depending on the feedstock preparation. For both curves a two-stage character of melting is clearly visible. It results from the melting of two thermodynamically different phases: eutectic mixture and austenite. It has a direct impact on the slope of the curve $\left(\frac{d\vec{f}_L}{dT}\right)_{30\%}$ and $\left(\frac{d\vec{f}_L}{dT}\right)_{50\%}$. It may also be observed that the range of melting eutectic mixture $(T_e - T_S)$ in steel after modification is 19°C higher in the sample which underwent plastic deformation. These differences may result from the presence of high melting chromium borides and carbides and lower melting iron containing eutectic mixture [27]. The temperature ranges $\Delta\vec{T}_{40-20\%}$ and $\Delta\vec{T}_{60-40\%}$, are narrower for the steel after modification compared to the steel which underwent plastic deformation. Solidus and liquidus temperatures as well as $\vec{T}_{30\%}$ and $\vec{T}_{50\%}$ are lower for the modified steel, what may be caused by iron containing eutectic mixture of borides and carbides [27]. Boron additions decreased characteristic temperatures which is accordance with Fe-B-C and Cr-B-C phase diagrams presented in [26, 27].

3.2. Characterization of microstructure

3.2.1. X210CrW12 steel after hot rolling

In the thixoforming process it is important that the metal slurry has globular grains surrounded by a liquid phase. Due to its high temperature, thixoforming is used for steel more often than other semi-solid processing methods e.g. rheoforming. Accordingly, the feedstock structure is prepared in a solid state by the SIMA method, which consists in plastic deformation of the ingot above the recrystallization temperature [12]. This method allows the use of commercially available rods as feedstock after their extrusion, forging and rolling. Figure 2a shows the microstructure of X210CrW12 steel raw material after hot rolling at 1020°C and annealing. Bands of primary and secondary carbides formed due to plastic deformation in the ferritic matrix can be observed in the microstructure. The investigated material belongs to ledeburite steel grade because the primary carbides which were precipitated during solidification form an eutectic mixture. The high content of alloying elements and carbon leads to the formation of M_7C_3 chromium carbides with hexagonal lattice, and $M_{23}C_6$ with regular lattice [22]. Average hardness of feedstock prepare by SIMA was 220 HV_5.

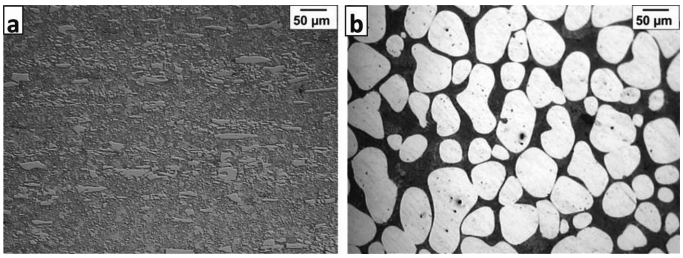

Fig. 2. Microstructure of X210CrW12 steel; **a)** hot rolled feedstock for thixoforming, **b)** heated up to 1230°C/5min and cooled in water

In order to determine whether the globular structure in X210CrW12 steel (feedstock preparation by SIMA) will be present in semi-solid range, the samples were heated to 1230°C and soaked for 5 minutes, and then cooled down in water. Figure 2b shows microstructure consisted of homogenous globular grains of solid solution (solid phase in semi-solid range) with average size of 57 μm, surrounded by eutectic mixture. Globular grains consisted mainly of austenite while carbides and ferrite were located in the eutectic mixture [22, 24]. On the basis of an image analysis the amount of the eutectic mixture was estimated at 18±1% (liquid phase in semi-solid range). Metallographic analysis of liquid fraction estimate corresponds with DSC analysis. The average size of grains is larger compared to the studies in which the same feedstock was used (with similar liquid fraction) [22, 23]. It is caused by longer heating rate and longer soaking time in semi-solid state. Qualitative chemical analysis confirmed a higher C, Cr and W content in the eutectic mixture than in the globular grains, which indicate the presence of carbides in the eutectic mixture [22]. Average hardness of feedstock prepared by SIMA and heated up to semi-solid state was 382 HV_5.

3.2.2. X210CrW12 steel after modification with boron

The method of feedstock preparation for SSP by modification can be more effective and less expensive than SIMA and RAP methods. Figure 3a shows the microstructure of X210CrW12 steel modified in the liquid state with 0.08% addition of boron in a sand mould. A fine globular structure of a solid solution surrounded by eutectic mixture can be clearly seen. According to the study by S. Sobula, [25] who investigated steel with similar chemical composition, grains of solid solution consist mainly of perlite.

In order present the positive influence of boron on the microstructure of X210CrW12 feedstock, samples without boron were cast. Figure 3b shows microstructure of unmodified X210CrW12 steel. A typical coarse dendritic strucutre with eutectic mixture is visible. This feedstock is not suitable for semi-solid processing.

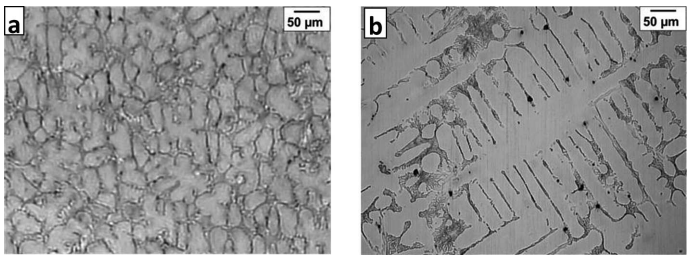

Fig. 3. **a)** Microstructure of the as cast X210CrW12 steel with added boron a feedstock for thixoforming **b)** Microstructure of the as cast X210CrW12 steel without boron

Figure 4 shows an X-Ray analysis of the feedstock – X210CrW12 steel with the boron addition (1). It can be seen that the raw material consists mainly of ferrite and M_7C_3 carbides as well as a small amount of austenite. Average hardness of feedstock was 485 HV_5.

Additionally figure 4 shows an X-Ray diffraction plot of the X210CrW12 steel feedstock with the boron addition after heating up to 1230°C/5min and cooling in water (2). It confirms the presence of austenite and M_7C_3 carbides. Such a considerable amount of austenite is connected with the increased contents of Cr and C in the solid solution stabilizing

the austenite, and it results also from the rapid cooling from the solid-liquid range.

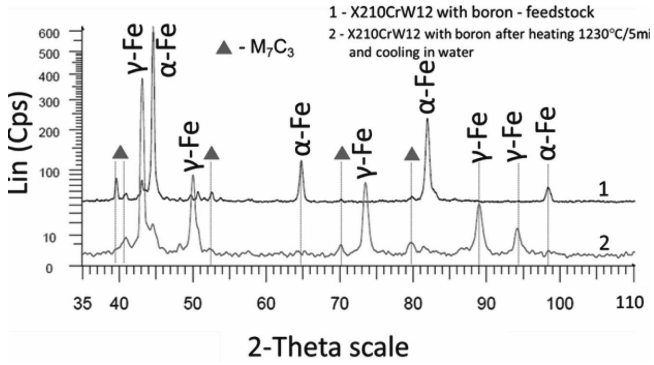

Fig. 4. X-ray diffraction curves of X210CrW12 steel with boron – feedstock samples (1) and after heating up to 1230°C/5min and cooling in water (2)

Figure 5 shows microstructure of X210CrW12 steel with boron after heating up to semi-solid range – 1230°C, which corresponds to 28% of liquid phase according to DSC studies. Quantative metallography analysis enabled to estimate the fraction of eutectic mixture at 29%, (which in semi-solid range exists as a liquid phase). A larger amount of a liquid phase (at lower temperature) in comparison to unmodified steel is caused by the presence of boron which leads to a decrease in melting temperature [26].

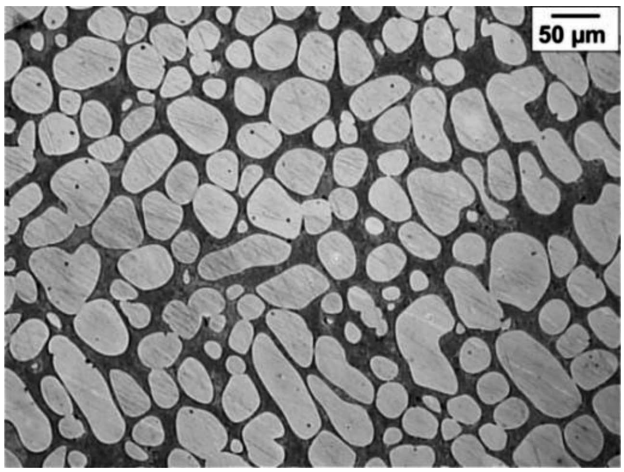

Fig. 5. Microstructure of X210CrW12 steel modified with boron, heated up to 1230°C and quenched in water

A globular microstructure with the average grain size 46 μm is surrounded by an eutectic mixture. One can observe a smaller grain size of steel after modification and heating up to the semi-solid state as compared to the steel prepared by SIMA. It can be caused by the presence of a high temperature borides which act of nuclei for grain formation. The presence of a high amount of borides and carbides is responsible for a decrease in the grain growth during heating to a semi-solid state [1, 28]. Average hardness of feedstock after heating to semi-sold range was 340 HV_5. Lower average hardness compared to the feedstock obtained by SIMA was caused by presence of smaller amount of carbides and borides in the eutectic mixture.

4. Conclusions

1. Hot plastic deformation (SIMA) and modification of molten metal by boron additions appeared to be effective ways of feedstock preparation for the thixoforming process.
2. Addition of boron in the amount of 0.08% to X210CrW12 steel caused a decrease in solidus-liquidus temperature and extension of melting range of eutectic mixture in relation to unmodified steel with the same chemical composition.
3. Microstructure of X210CrW12 steel samples obtained by SIMA after cooling from the temperature of 1230°C shows 18% of the liquid phase and consists of austenite globular grains with the average size of 57 μm, surrounded by an eutectic mixture.
4. Microstructure of X210CrW12 steel modified with boron cooled form the semi-solid range at 1230°C shows 28% of the liquid phase and consists from a fine globular grains of austenite of average size of 46 μm, surrounded by an eutectic mixture.

Acknowledgements

The research was supported by Polish science financial resources Applied Research Programme of the National Centre for Research and Development in Poland, "Developing a technology of producing complex elements by steel thixoforming", No. PBS1/B5/22/2013, the authors would like to thank Professor J. Głownia for preparing melts and their valuable comments.

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Received: 15 February 2013.