Characterisation of weld deposits using as filler metal a high entropy alloy

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The concept "hyperentropic alloys" refers to the development of one special metal matrix in which all the chemical elements participate in molar equivalent reports, without one of them to be the matrix. Such alloys have special characteristics such as high hardness combined with toughness and plasticity, which can be obtained depending on the constituents and thermal regime applied after elaboration. In this paper we present some results obtained as welding deposition of a hyperentropic alloy, upon unalloyed steel support (S 275 J2). The weld deposition has been heat treated of aging annealing at 600 °C and 900 °C for 4 and 6 hours. To reveal microstructural aspects were analyzed welded areas, by optical and electronical microscopy and then were made microhardness measurements. It was found that by the fast cooling of hyperentropic alloys it can achieve high values of hardness but low plasticity, and by applying heat treatments, can be obtained different pairs of hardness and plasticity, depending on the dedicated application. The hardness values of weld deposit are 3.5 times higher than those of the base material, without cause hardening of heat affected zone.

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1. Introduction

Most traditional metal alloys are based on a metallic element that represent metallic matrix such as iron, aluminum, copper, titanium, nickel or magnesium, in which are dissolved other alloying elements in much smaller quantities. Such alloys are usually composed of one or two main elements, which determine the main structural properties, physico-chemical or mechanical characteristics. The small addition of other micro-alloying elements allows improving some of these characteristics.

During the period 1995 - 2000, there has been developed a new concept, different from that of obtaining the conventional alloys, which permit the development of many other alloys family [1]. The new series of alloys have been called "high entropy alloys" because the mixing entropies are larger than those of the traditional alloys in liquid state or in solid solution. By definition, each high-entropy alloy contains at least five main metallic elements, with concentrations between 5 and 35 at%. Recent developments in high entropy alloys have shown that they have multiple properties and can therefore be used in promising applications [1].

High entropy alloys (HEA) are composed of n major alloying elements, with $n \ge 5$, having molar equivalent reports or nearly equivalent molar reports, leading to the formation of solid solution phases with simple network, type of c.f.c. or c.v.c., nano-structures and even amorphous state. Therefore, HEA are solid solutions with high strength, good thermal stability, and greater quenching capacity than conventional alloys, combined with superior resistance to various environmental conditions [2].

It is known that when the main alloying element has a limited solubility, mechanical strength can increase due to solid solution hardening tendency. For a particular structure, if is kept constant the composition of the alloy it can get a combination of strength and plasticity characteristics by applying different heat treatment procedures. Increasing the amount of a particular alloying element in the alloy determine the formation of some typical intermetallic compounds, due to limited solubility in the solid state, that lead to the increase of resistance and hardness but with the increase the fragility [3, 4]. To achieve a homogeneous structure solution, a new design concept of multi-component metal alloy must be applied. Besides the main elements constituting the alloy hiperentropic, small amounts of other elements can be added such as Nb, Zr, Ti, in order to optimize the adhesion conditions at the interfaces and to improve mechanical characteristics (Fig. 1) [5].

In the studies on certain types of high entropy alloys were analyzed in literature, the effects of adding certain chemical elements (such as Al, B, N, Cr, Ti, Fe and V) on the microstructure and mechanical properties [6, 7, 8]. Alloying elements with different values of network parameters can affect both crystalline microstructure and properties of these alloys as well. So far, have not been fully clarified all these effects and especially is not know exactly if there is a correlation between the electronic configuration of alloying elements and the overall microstructure of high-entropy alloys.

Mechanical characteristics of high entropy alloys can be improved by applying heat treatment of aging [2] below 645 °C, the compressive strength values being in the domain of 1750 - 2100MPa. If the treatment temperature increases to 900° C, the yield strength decreases but elongation is improved up to 27 %.

2. Experimental procedure

2.1. Getting the high entropy alloys

Metal alloys with high entropy were obtained in laboratory ERAMET of UPB-SIM, using a vacuum arc remelting furnace (VAR), model MRF ABJ 900 VAR. By calculating of the percentage participation of each element, the recipes for hyper-entropic base alloys are established, that contain molar equivalent percents of Al, Cr, Co, Ni, Fe. Were conducted several test samples in the form of rods, which later served as filler material for welding deposition (Fig. 1). The alloy was melted in metallurgical unit 3 times on each surface separating, using inert atmosphere of argon, in order to obtain an adequate homogeneity.



Fig. 1. High entropy alloy rods.

2.2. Welding deposition and heat treatments

To achieve deposition by welding, rods of hiperentropic alloy were used, obtained under argon medium and casted in water-cooled copper mold. Weld deposition of high-entropy alloy layers was performed on S 275 J2 steel support with TIG welding process, using a current source PRESTOTIG 210 and welding current value of 90A. On visual examination it was found that deposition has good adhesion to the support material.

After welding, the samples for metallographic analysis and hardness measurement were taken, and some of these for the aging heat treatment at 600 $^{\circ}$ C for 4 and 6 hours and at 900 $^{\circ}$ C for 6 hours.

Heat treatments have performed in Nabertherm LT 15/12/P320 furnace with programmable diagram for thermal regime. Heating rate was 20 °C/min and cooling was performed in air for sample maintained for 4 hours, and with the furnace for the sample maintained for 6 hours.

3. Microstructural analysis

Samples were prepared for metallographic analysis by electron microscopy and SEM, in accordance with the metallographic sample preparation procedure of laboratory LAMET from UPB [9]. Using examination by optical microscopy at different magnifications has revealed the dendritic morphology of high entropy alloy, in as-cast form (Fig. 2).



Fig. 2. Optical microscopy images of HEA1 alloy (Al, Cr, Fe, Co, Ni). Dendritic microstructure and fine precipitates on grain boundaries and in the body: a) 200x; b) 500x. (Laboratory LAMET, UPB).

At high magnification (10000 X) the microstructure of high entropy alloy has a very fine dendritic network, with clear delineation of grain boundaries, having the width of about 240 μ m (Fig.3).

Weld deposit aspect was highlighted in cross section, the angle between the weld seam and metal support having the 36° value. It shows a good adhesion between the weld deposit and the non-alloy steel substrate, with formation of zones of mixing, less extensive through the weld (Fig. 4.a).





Fig. 4.b. Macroscopic appearance of weld deposit with high entropy alloy before applying heat treatment (x100).



Fig. 3. High entropy alloy microstructure. SEM microscopy. (x10000).



Fig. 4.a. Macroscopic appearance of weld deposit with high entropy alloy before applying heat treatment (x50).

The heat affected zone is narrow, with thickness of $600 \ \mu m$, and the grains experienced a slight increase in diameter due to the welding heat cycle (Fig. 4b).

After maintaining at the temperature of 600°C for 4 hours was observed a thickening of fusion line (width about 11 microns), and the accumulation of alloying elements, diffused from base material or weld deposit (Fig. 5.a, Fig. 5.b).

Prolongation of the maintaining time at heat treatment up to 6 hours and furnace cooling, caused further thickening the fusion line, with doubling its width up to 22 μ m (Fig. 6.a, Fig. 6.b and Fig. 7.a, Fig. 7.b).

Keeping the heat treatment temperature of 900°C determined some decarburization effects in the HAZ, heat affected zone having an extension up to 400 microns (Fig. 8).



Fig. 5.a. Fusion line with elemental accumulation due to heat treatment at 600°C for 4 hours.



Fig. 5.b. Fusion line with elemental accumulation due to heat treatment at 600°C for 4 hours.



Fig. 6.a. Fusion line with elemental accumulation, due to heat treatment at 600 °C for 6 hours.



Fig. 7.a. Fusion line with elemental accumulation, due to heat treatment at 900°C for 6 hours.



Fig. 7.b. Fusion line with elemental accumulation, due to heat treatment at 900°C for 6 hours.



Fig. 6.b. Fusion line with elemental accumulation, due to heat treatment at 600 °C for 6 hours.



Fig. 8. Heat affected zone for heat treated sample at 900°C/6 hours/furnace cooled.

4. Microhardness measurements

The microhardness measurements for high entropy alloy were performed using a Shimadzu HMV 2T apparatus and the values are presented in Table 1.

Table 1.	Microhar	dness va	lues HV0.1	for
	HEA 1	AlCrFeC	CoNi	

Sample	Measurement zone	Average value
HEA 1- AlCrFeCoNi	Bulk	562
	Base material S275J2	157
Weld deposit	Heat affected zone	169
	Weld deposit with HEA 1 filler metal	593
	Base material	155
Heat treated at	Heat affected zone	109
600°C/4hours/	Weld deposit with	648
air	HEA 1 filler metal	
Heat treated at	Base material S275J2	160
600°C/6hours/	Heat affected zone	132
furnace	Weld deposit with HEA 1 filler metal	652
	Base material S275J2	158
Heat treated at	Heat affected zone	112
900°C/6hours/ furnace	Near fusion line in weld deposit	563
	Weld deposit with HEA 1 filler metal	388

From the analysis of Microhardness results it can be concluded that hardness of weld deposit increases by applying of an annealing heat treatment at 600°C, but the increasing of the maintaining time does not modify significantly this hardness.

By increasing the heat treatment temperature from 900 °C has been obtained the further decrease of hardness in weld deposit. Has been noted also a decrease of HAZ hardness for the sample annealed in comparison with samples welded, probably due to the diffusion phenomena trough the fusion line.

5. Conclusions

Experimental alloy with high entropy have hardness features over 3.5 times higher than that of a carbon steel used for structural applications.

The use of this alloy as material for loading by welding allows obtaining the layers with special characteristics, including wear resistance and impact resistance, corrosion resistance, etc., depending on the chemical composition designed.

Deposition welding can be done with conventional methods (TIG) in a protective atmosphere of inert gas, the resulting adhesion and wetting characteristics at the base material surface being appropriate.

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