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Effect of carbon content on cryogenic mechanical properties of CoCrFeMnNi high entropy alloy

A Semenyuk*, M Klimova, D Shaysultanov, R Chernichenko, S Zherebtsov and N Stepanov

Belgorod State National Research University, Pobeda, 85, Belgorod, 308015, Russia

*Corresponding author: semenyuk@bsu.edu.ru

Abstract. The effect of the carbon content (0-2 at.%) on the structure and mechanical properties at room and cryogenic temperatures of CoCrFeNiMn-based high entropy alloys with reduced Cr concentration was studied. The as-cast alloys were cold rolled to a thickness reduction of 80% and annealed at 800°C for 1 hour. As a result, a fully recrystallized microstructure with a grain size of 6.4 μm was produced in the carbon-free alloy. The recrystallized grain size was much smaller (1.5 μm in the alloy with 2.0 at.% of C) due to the pinning effect of the precipitated $M_{23}C_6$ carbides. The yield strength of the alloys increased with an increase in the carbon concentration from 313 MPa to 636 MPa, while the elongation to fracture slightly decreased from 56% to 43%, respectively, in the alloys with 0 and 2 at.% of C. A decrease in the test temperature to 77K resulted in a significant increase in both the strength and ductility of the alloys. The alloys had high values of impact toughness of 140 J/cm^2 and 85 J/cm^2, respectively, in the alloys with 0 and 2 at.% of C. A decrease in the testing temperature did not have a noticeable effect on the impact toughness.

1. Introduction

High-entropy alloys (HEAs) represent a new class of metallic materials with promising properties. The first mentions of HEAs date back to 2004 [1]; in several works, they are referred to as multicomponent equiatomic alloys. According to the initial definition of HEAs, these are the alloys that consist of at least 5 elements, and the amount of each element should be 5-35 at.%.

Alloys based on 3d transition metals are among the most studied HEAs families. They usually crystallize with a face-centered cubic (FCC) structure and have attractive mechanical properties. Alloys of the CoCrFeMnNi system exhibit high ductility and impact toughness at room temperature [3]. Their mechanical properties are even better at cryogenic temperatures, which makes them attractive for cryogenic applications. However, CoCrFeMnNi-based alloys have relatively low strength [4]. One of the most effective ways to increase strength is alloying with interstitial elements, in particular, carbon [5-7]. Carbon-doped HEAs can benefit both from interstitial solid solution hardening due to dissolved carbon atoms and from precipitation hardening due to the formation of carbides [8]. The equilibrium solubility of carbon in the CoCrFeMnNi solid solution is low due to the presence of a strong carbide-forming element, Cr. A decrease in the molar concentration of chromium can potentially increase the equilibrium solubility of carbon. Meanwhile, carbide particles can also affect the fcc grain size. It was shown in several works [9-10] that secondary phases in CoCrFeNi (Mn, Al, C) alloys can effectively restrict grain growth and promote the formation of a fine-grained microstructure. The fine grain size can also be beneficial for strength. However, the effect of carbon on the cryogenic mechanical properties of CoCrFeMnNi alloys, especially on the impact toughness, at cryogenic temperature is poorly studied. Therefore, in this work, we studied the tensile mechanical properties and impact toughness at room and cryogenic temperatures of CoCrFeMnNi high-entropy alloys with a different carbon content (x = 0, 0.5 and 2.0 at.%) after thermomechanical processing.

2. Materials and methods

CoCrFeMnNi-based high entropy alloys with a reduced concentration of Cr and different carbon concentration (x = 0, 0.5, and 2.0 at.%; further denoted as C0, C0.5, and C2.0 alloys respectively) were produced by vacuum induction melting. The measured chemical composition of alloys is presented in Table 1. The as-cast samples were cold rolled at room temperature to a thickness reduction of 80%. The samples then were annealed in a muffle furnace in an air atmosphere at temperatures of 800°C for 1 hour, followed by cooling in air.

Table 1. Measured chemical composition of the alloys depending on the carbon concentration.

	Concentration of elements, at.%					
	Co	Cr	Fe	Mn	Ni	C
C0	23.29	6.22	23.90	23.09	23.46	0.03
C0.5	23.17	6.42	23.97	23.67	22.24	0.53
C2.0	23.42	6.23	22.41	22.02	23.82	2.11

The microstructure of the alloy was studied using scanning (SEM) and transmission (TEM) electron microscopy in the RD-ND plane (perpendicular to the transversal direction). SEM studies were carried out a using FEI Quanta 600 FEG microscope equipped with a backscattered electron (BSE) detector. TEM investigations were conducted using a JEOL JEM-2100 microscope with an accelerating voltage of 200 kV equipped with an EDS detector. Selected area electron diffraction (SAEDs) patterns were used for the phase identification and results of EDS – for chemical analysis. Tensile tests were carried out on an Instron 5882 universal electronic tensile testing machine with a strain rate of 1×10^{-3} s^{-1} at room (293K) and cryogenic (77K) temperatures using samples with a dimension of $6\times3\times1.5$ mm^3. The KCV impact toughness was determined on an Instron IMP460 pendulum impact machine using samples with a dimension of $2 \times 8 \times 55$ mm^3 and with a V-notch in the center at the same temperatures.

3. Results

The microstructure of the program alloys after cold working and annealing at 800˚C is shown in Figure 1. A fully recrystallized microstructure with many annealing twins was observed. The C0 alloy (Figure 1a) had a single-phase structure with a grain size of 6.4 μm. The addition of carbon promoted the precipitation of the Cr-rich $M_{23}C_6$ carbides. The precipitation of the carbides resulted in a decrease of the recrystallized fcc grain size. For instance, in the C0.5 alloy (Figure 1b) with 1.5% of carbides the grain size was 5.2 μm, while in the C2.0 alloy (Figure 1c) the volume fraction of carbides increased to 7.4% and the grain size decreased by 1.6 μm. The size of the carbide particles increased from 89 nm to 117 nm in the C0.5 and C2.0 alloys, respectively. Carbides were found both along the grain boundaries and in grain interiors.

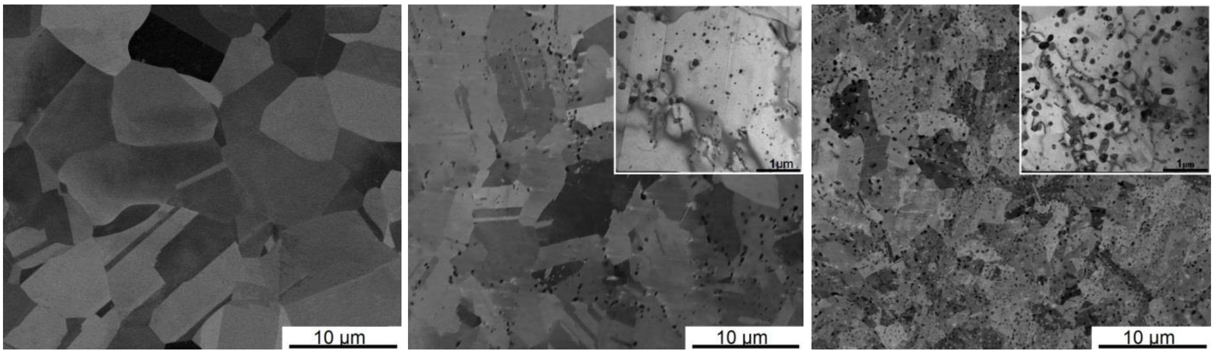

Figure 1. SEM-BSE images of the microstructure of the CoCrFeNiMn alloys with different carbon contents (x): C0 (a); C0.5 (b); C2.0 (c) after annealing at 800°C.

The tensile stress-strain curves of the alloys obtained at room (293 K) and cryogenic (77 K) temperatures are shown in Figure 2. At 293 K the yield strength increased with an increase in the carbon content from 313 MPa for the C0 alloy to 636 MPa for the C2.0 alloy (Table 2). The ductility decreased as the carbon concentration increased from 56% for the C0 alloy to 43% for the C2.0 alloy. Decreasing the testing temperature to 77 K led to a simultaneous increase in both strength and ductility of the alloys. The yield point slightly increased from 460 MPa in the C0 alloy to 480 MPa in the C0.5 alloy and then raised sharply to 786 MPa in C2.0 the alloy.

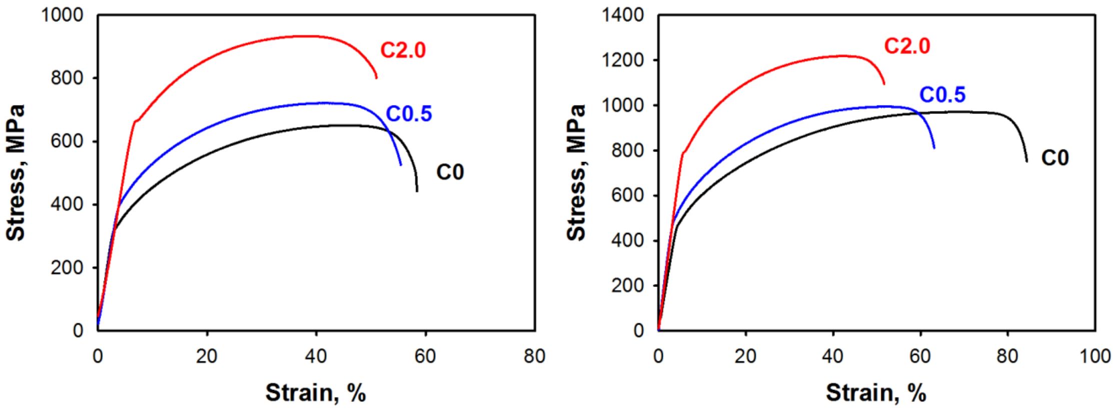

Figure 2. Tensile stress-strain curves of the CoCrFeMnNi alloys with different carbon content after cold rolling and annealing at 800°C obtained at 293 K (a) and 77 K (b).

Table 2. Mechanical properties of the CoCrFeMnNi alloys with different carbon contents (x) of after cold rolling and annealing at 800°C obtained at room and cryogenic temperatures

Temperature	293 K					77 K				
Alloy	YS, MPa	US, MPa	TE, %	UE, %	KCV, J/cm^2	YS, MPa	US, MPa	TE, %	UE, %	KCV, J/cm^2
C0	313	651	56	41	142	460	970	76	57	140
C0.5	381	721	52	36	119	480	994	62	48	130
C2.0	636	933	43	29	85	786	1218	52	39	86

Impact toughness testing has revealed the following trends: (i) the impact toughness decreased with increasing carbon content. For instance, at room temperature, the respective values of KCV for the C0 and C2.0 alloys were 140 J/cm^2 and 85 J/cm^2. Besides, only the C2.0 alloy completely disintegrated into two parts, which indicates a low resistance to crack propagation. (ii) The testing temperature had a rather weak effect on the impact toughness, for example, the KCV values obtained at 293K and 77K for the C0.5 alloy were 119 J/cm^2 and 130 J/cm^2, respectively. Figure 3 shows the fracture surfaces of the program alloys after impact tests at 293 K (a, b, and c) and 77 k (d, e, and f). The C0 alloy showed ductile fracture appearance with coarse dimples both at room and cryogenic temperatures. The C0.5 and C2.0 alloys also showed a ductile fracture, but with smaller dimples. At 77 K in the C2.0 alloy, brittle fracture takes place near the notch (not shown).

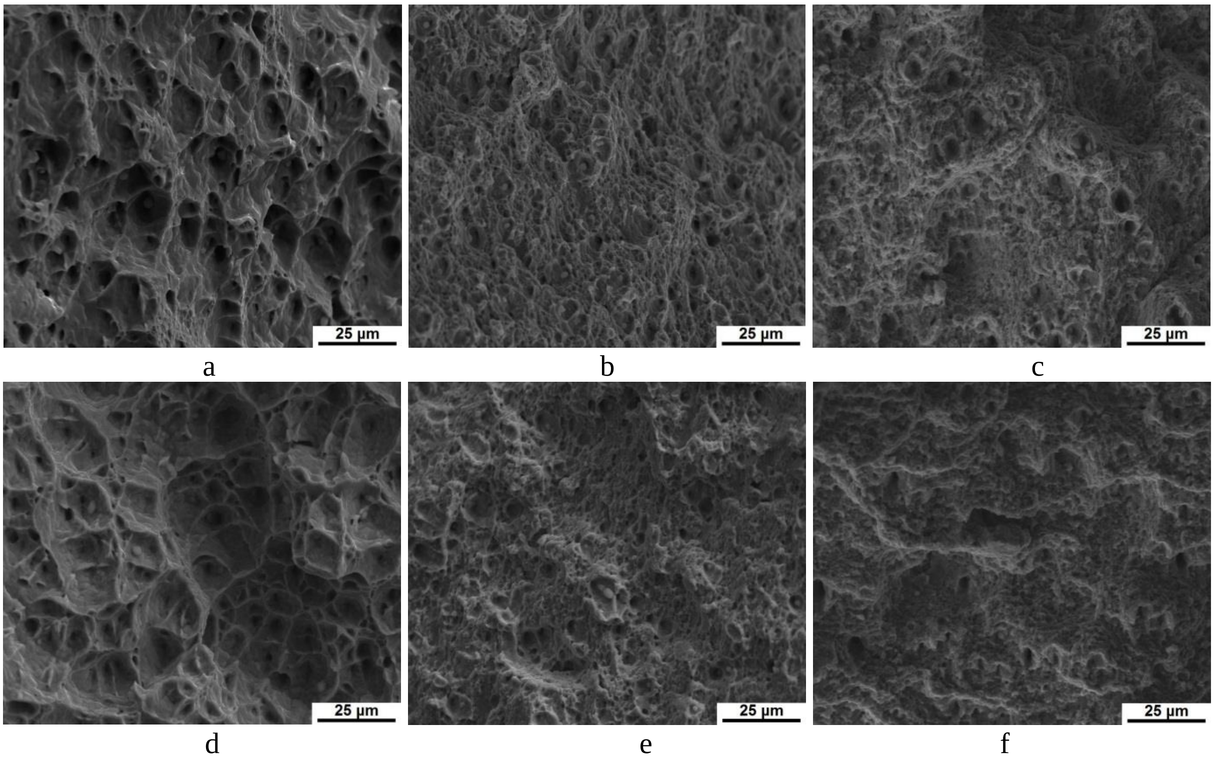

Figure 3. Fractography of the CoCrFeMnNi alloys with different carbon content after impact tests at 293K (a-c) and 77K (d-e): C0 (a, d); C0.5 (b, e); C2.0 (c, f).

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